

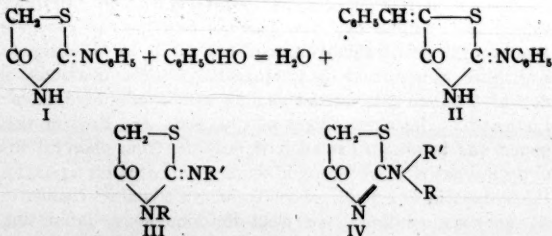
AMERICAN CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University]

CCl.—DESMOTROPISM IN THE PSEUDOTHIOHYDANTOINS

BY TREAT B. JOHNSON AND JOSEPH A. AMBLER

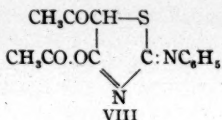
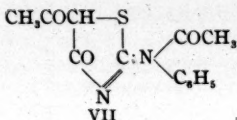
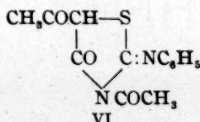
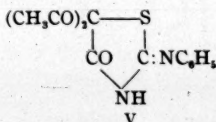
It is known that certain pseudothiohydantoins, which contain the thioglycollide grouping $\text{—S.CH}_2\text{CO—}$, behave in a tautomeric manner with respect to their reactions with aldehydes and acetic anhydride. For example, the methylene hydrogens in the stable arylhydantoins (I), and also those of the disubstituted pseudothiohydantoins, (III) and (IV), are capable of reacting with aldehydes in a manner similar to that of benzyl cyanide,¹ forming condensation products corresponding to the hydantoin² (II).



¹ Meyer: Ann. Chem. (Liebig), 250, 124.

² Wheeler and Jamieson: J. Am. Chem. Soc., 25, 366.

On the other hand, the stable hydantoins (I) react smoothly with acetic anhydride, forming stable diacetyl derivatives.¹ No definite constitution, however, was assigned to these diacetyl compounds, but it was shown that they do not behave as acetoacetic acid derivatives. In other words, the hydrogens of the methylene group (CH_2) are not directly replaced by both acetyl groups as represented in formula (V) or by one acetyl radical as represented in the two hydantoins (VI) and (VII). This was established by the fact that these diacetyl



derivatives are insoluble in alkali. Formula (VIII) is not to be considered since it represents an unstable structure—an imido acid anhydride,² which would be expected to rearrange into its stable isomer (VI).

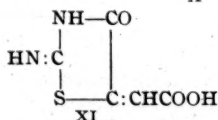
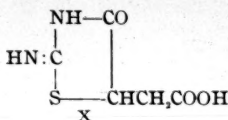
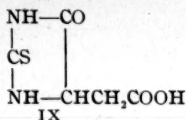
It follows, therefore, from these results that the structure of these pseudothiohydantoins (I) cannot be established by acetylation or by their behavior towards aldehydes. In other words, the chemical evidence does not enable us to conclude whether the pseudothiohydantoin nucleus is to be assigned a definite constitution or whether its twofold character is due to the fact that we are dealing with a case of dynamic isomerism. The chief object of the work described in this paper was to obtain evidence, if possible, from observations of optical activity, which would serve to indicate that a pseudothiohydantoin is capable of undergoing a dynamic change in an aqueous solution. We shall describe some interesting

¹ Wheeler and Johnson: *THIS JOURNAL*, **28**, 121.

² Wheeler and Johnson: *Ibid.*, **30**, 24.

results which we have obtained by examination of the rotation of an active salt of pseudothiohydantoinacetic acid.

If one considers only carbon substitution products and disregards also tautomeric and imido acid anhydride modifications theoretically possible, there are two thiohydantoinacetic acids, viz., the normal acid, thiohydantoin-4-acetic acid (IX), and the pseudo acid, pseudothiohydantoinacetic acid (X), which we used in our work. Of these two acids this pseudo form (X) is the only one which has hitherto been described in the literature. It was first prepared by Tambach¹ by the action of thiourea on bromosuccinic acid. It was later synthesized by Andreasch² by the addition of thiourea to maleic or fumaric acids, by the action of cyanoamide on thioaspartic acid, and also by the reduction of dehydrothiohydantoinacetic acid (XI) with sodium amalgam.³ A description of the unknown acid



(IX) has been given in a recent publication from this laboratory.⁴

Regarding the constitution of pseudothiohydantoinacetic acid Andreasch⁵ writes as follows: "Die Thiohydantoinessigsäure enthält übrigens ein asymmetrisches Kohlenstoffatom und kann daher in ihren optischen Isomeren existieren; auf eine eventuelle optische Activität wurde nicht geprüft." So far as the writer is aware, Andreasch made no attempts later to obtain the active modifications of this acid. We now find

¹ Ann. Chem. (Liebig), **220**, 233 (1894).

² Monats., **16**, 789.

³ *Ibid.*, **16**, 78.

⁴ Johnson and Guest: *THIS JOURNAL*, **48**, 103.

⁵ *Loc. cit.*

that this acid combines with the active base brucine, forming a stable salt which is extremely soluble in water. It was easily purified by crystallization from 95 per cent. alcohol. We have subjected this salt to a systematic fractional crystallization and made a very thorough study of its rotatory power in aqueous solution. All attempts, however, to separate two optical modifications of the salt were without success. The salt was found to have a definite specific rotation, in aqueous solution, of $[\alpha]_D^{20} -12^{\circ}.65$. We obtained no evidence of the existence of the other active modification. Furthermore, when this active salt, $[\alpha]_D^{20} -12^{\circ}.65$, was decomposed by hydrochloric acid, the original inactive pseudothiohydantoinacetic acid, melting at $245-250^{\circ}$, was obtained. These results therefore indicate that pseudothiohydantoinacetic acid does not contain a true asymmetric carbon atom.

We have now made the interesting observation that a solution of the brucine salt in water does not retain its original activity, while a crystalline specimen showed no change in activity. In other words, the salt exhibits mutarotation in this solvent. In fact, the specific rotation $[\alpha]_D^{20} -12^{\circ}.65$ given above is the average of a series of measurements, which were made immediately after dissolving the salt in water. If the aqueous solution is allowed to stand at ordinary temperature the rotatory power begins to increase slowly and finally attains a constant maximum value of $[\alpha]_D^{20} -25^{\circ}.0-25^{\circ}.2$. The rapidity with which this transformation takes place increases in marked degree with the rise in temperature. At the ordinary laboratory temperature of $20^{\circ}-25^{\circ}$ the change was complete after 72 hours, but on heating the solution to boiling the transformation is completed within a few minutes. It is an interesting fact that the relation of the initial to the final rotation is 2 : 1.

The cause of this interesting change is very probably to be found in the transformation of desmotropic modifications of the hydantoinacetic acid. Whether we are dealing here with a case of keto-enol desmotropy analogous to that observed by Dakin¹ in the case of the active hydantoins, or whether it

¹ THIS JOURNAL, 44, 48.

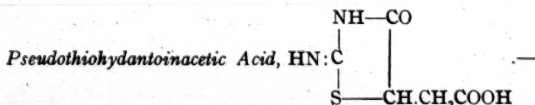
involves a change in the amidine linking of the hydantoin nucleus, must be decided by further work. These variations shown in specific rotation, however, do not depend on the phenomenon of hydrolytic dissociation because the specific rotation was always the same, $[\alpha]_D^{20} -12^\circ.6$ and $[\alpha]_D^{20} -25^\circ.0$, when the rotation was determined in solutions of different concentrations. By increasing the dilution, the number of active aggregations should be increased if the salt underwent hydrolysis, and, consequently, the specific rotation should be different for each concentration and the greatest in dilute solutions.

SUMMARY

The brucine salt of pseudothiohydantoinacetic acid is capable of undergoing a change in an aqueous solution, and this can be followed quantitatively by means of the polarimeter.

The variations in specific rotation are not due to the phenomenon of hydrolytic dissociation, but are probably in response to a desmotropic change in the pseudothiohydantoin nucleus of the salt.

EXPERIMENTAL PART



Andreasch¹ prepared this hydantoin by heating fumaric or maleic acid and an equivalent amount of thiourea with water in a closed vessel at 105° , and states that it decomposes at $210-212^\circ$ without melting. He qualifies this, however, as follows: "doch scheint die Schnelligkeit des Erhitzens für den Zersetzungspunkt maassgebend zu sein, da mitunter auch ein höherer Zersetzungspunkt (218°) beobachtet wurde." Tambach¹ likewise gives the decomposition point as 210° . We prepared the acid in the following manner: Five grams of fumaric acid and 3.3 grams of thiourea were ground together and the powder suspended in 4 cc. of water. This was then

¹ Loc. cit.

heated, in a small flask, on a boiling water bath for two days. The solid did not dissolve at any period of the reaction. After the reaction was complete the hydantoin was purified by crystallization from boiling water. It separated on cooling in beautiful, prismatic crystals, which decomposed from 245°–250° with effervescence. There was no evidence of melting at 210°. Moreover, we prepared the acid by Tambach's method and obtained the same acid melting at 245°–250°. If the sulphuric acid bath is heated rapidly the decomposition point can be raised as high as 260°. The yield of purified acid was 6 grams, or 72 per cent. of the theoretical. The isomeric thiohydantoinacetic acid¹ melts at 222° with effervescence. Nitrogen determinations (Kjeldahl):

	Calculated for $C_5H_6O_3N_2S$	I	II	Found III	IV
N	16.09	15.8	15.8	15.63	15.87

Hydrochloride, $C_5H_6O_3N_2S.HCl$.—Pseudothiohydantoinacetic acid possesses weak basic properties. The double platinum chloride salt has been made by Tambach, but it undergoes decomposition in water, giving the original hydantoin. We succeeded in isolating the hydrochloride in the following manner: A small amount of the hydantoin was dissolved in 10 cc. of boiling hydrochloric acid and the solution cooled and allowed to stand. The hydrochloride deposited in the form of prisms arranged in radiating groups. These were filtered off and dried in a desiccator over potassium hydroxide. The salt melts at 210°–212° with effervescence and is dissociated by cold water into hydrochloric acid and the hydantoin melting at 245°–250°. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_3N_2S.HCl$	Found
N	13.33	13.09

Hydrolysis of the Pseudothiohydantoinacetic Acid.—One gram of the hydantoin acid, melting at 245°–250°, was boiled with 20 cc. of hydrochloric acid for two hours. The solution was then concentrated and cooled, when prisms separated. They were filtered off and purified by recrystallization from hot

¹ Johnson and Guest: *Loc. cit.*

water. The compound melted at 169° – 170° and was identified as dioxythiazoleacetic acid.¹

Sodium Salt, $C_5H_5O_3N_2SNa \cdot 3H_2O$.²—This salt was obtained from our acid melting at 245° – 250° ; 0.5019 gram of the acid was dissolved in 36.3 cc. of a 0.1 N sodium hydroxide solution and this then concentrated on the steam bath. On cooling, the sodium salt was obtained in the form of large, flat, tabular crystals.

Water determination:

I. 0.4674 gram salt lost at 100° – 110° 0.1031 gram H_2O .

	Calculated for $C_5H_5O_3N_2SNa \cdot 3H_2O$	Found
H_2O	21.60	22.0

Barium Salt, $(C_5H_5O_3N_2S)_2Ba \cdot H_2O$.—One gram of our pseudothiohydantoinacetic acid was dissolved in 72.3 cc. of 0.1 N sodium hydroxide solution and this solution then concentrated to a volume of about 10–15 cc. The required amount of barium chloride, $BaCl_2 \cdot 2H_2O$ (0.7012 gram), dissolved in water, was added to this solution. The resulting mixture was heated to boiling, filtered from a trace of barium carbonate and the solution concentrated and cooled. The barium salt then separated. This was dried, for analysis, in the air.

Water determination: Loss at 110° – 120° .

I. 0.8110 gram substance lost 0.0317 gram of H_2O .

Barium determination:

II. 0.7793 gram substance gave 0.3076 gram $BaCO_3$.

	Calculated for $(C_5H_5O_3N_2S)_2Ba \cdot H_2O$	I Found	II
H_2O	3.59	3.91	...
Ba	28.40	..	28.35

Active Brucine Salt, $C_5H_5O_3N_2S \cdot C_{23}H_{28}O_4N_2$.—This salt was prepared by suspending 15 grams of the hydantoinacetic acid and 33.95 grams of Kahlbaum's brucine in water and then warming until a clear solution was obtained. The acid and base are practically insoluble in water while the salt is extremely

¹ Andreasch and Tambach: *Loc. cit.*

² Tambach: *Loc. cit.*

soluble. The aqueous solution was evaporated to dryness and the crude salt then purified by crystallization from 95 per cent. alcohol. It separated from this solvent in blocks which melted at 177° with effervescence. It was dried for analysis at 100° .

Nitrogen determination (Dumas method):

I. 0.1043 gram substance gave 8.6 cc. of N_2 at 18° and 765 mm. pressure.

	Calculated for $C_{21}H_{19}O_2N_2S.C_{22}H_{20}O_4N_2$	Found
N	9.8	9.58

The cinchonine and strychnine salts of pseudothiohydantoinacetic acid are extremely soluble in cold water.

Optical Rotation.—Attempts to resolve the acid into optical isomers by fractional crystallization of the brucine salt were without success. The specific rotation, in aqueous solution, was $[\alpha]_D^{20} -12.65^{\circ}$ and after a systematic crystallization of the salt from 95 per cent. alcohol we obtained no evidence of any other optical modification. When this active salt was decomposed by cold hydrochloric acid the original acid was obtained and was optically inactive. For example: some of the pure salt, having an initial specific rotation of $[\alpha]_D^{20} -12^{\circ}.6$, was dissolved in the least possible amount of water and hydrochloric acid added drop by drop until the hydantoinacetic acid deposited. The solution was then warmed gently to dissolve the brucine hydrochloride and the acid recrystallized from water to separate all traces of the brucine salt. The acid melted at 245° – 250° as before; 0.3568 gram of it was then dissolved in cold concentrated hydrochloric acid (25 cc.) and the solution diluted to 50 cc. with water. This showed no optical activity even after long standing.

In order to determine whether the salt exhibits mutarotation, which would serve to indicate a tendency to undergo change into desmotropic modifications, its rotatory power in water solution was determined immediately after solution and also after the solutions had stood for different periods. The results obtained are given in Table I.

Table I.

Rotatory power in water solution. $c = 5$, $l = 1$, temperature = 20°

Crop A

	$[\alpha]_D^{20}$
Rotation after 2-3 hours	$-15^{\circ}.74$
Rotation after 72 hours	$-24^{\circ}.8$
Rotation after 216 hours	$-24^{\circ}.8$
Rotation after 336 hours	$-25^{\circ}.0$

Crop B

Immediate rotation	$-12^{\circ}.76$
Rotation after 72 hours	$-24^{\circ}.6$
Rotation after 168 hours	$-25^{\circ}.2$
Rotation after 264 hours	$-24^{\circ}.8$
Rotation after 346 hours	$-25^{\circ}.0$

Crop C

Immediate rotation	$-13^{\circ}.04$
Rotation after 72 hours	$-25^{\circ}.0$
Rotation after 144 hours	$-25^{\circ}.0$
Rotation after 240 hours	$-25^{\circ}.0$

Crop D

Immediate rotation	$-11^{\circ}.9-12^{\circ}.0$
Rotation after 72 hours	$-25^{\circ}.0$
Rotation after 144 hours	$-25^{\circ}.0$
Rotation after 240 hours	$-25^{\circ}.0$

The effect of heat on the rotatory power is shown by inspection of the results given in Table II.

Table II

Rotation in aqueous solution after heating to boiling and cooling.

$c = 5$, $l = 1$, temp. = 20°	$[\alpha]_D^{20} -25^{\circ}.2$
$c = 7$, $l = 1$, temp. = 20°	$[\alpha]_D^{20} -25^{\circ}.2$

NEW HAVEN, CONN.

June 1, 1912

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND CINNAMYLIDENE ESTERS

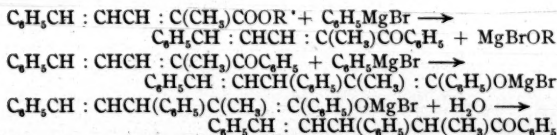
IV. REACTIONS WITH METHYL α -METHYLCINNAMYLIDENACETATE

BY MARIE REIMER AND GRACE POTTER REYNOLDS

The object of the series of investigations, of which the work described in this paper forms a part, was to study the effect of a second ethylene linkage on the reactivity of the system $C:C:C:O$. For this purpose the reaction chosen was that between the Grignard reagent and esters of cinnamylidenacetic acid and its α -substitution products.

In the present paper the results obtained with methyl α -methylcinnamylidenacetate are described.

With phenylmagnesium bromide the reaction consists in a replacement of the alkoxyl group of the ester by the phenyl group and addition, in the 1,4 position, of a second molecule of phenylmagnesium bromide according to the following equations:

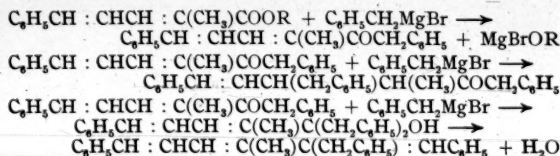


Two isomeric ketones, melting at 112° and 85° , respectively, are formed in this reaction. These ketones contain an ethylene linkage as well as two unequal asymmetric carbon atoms. If the isomerism were geometric, oxidation of the two ketones at the ethylene linkage should give rise to the same ketonic acid. It has been found, however, that the ketones give, on oxidation, isomeric ketonic acids. They are, therefore, racemic compounds.

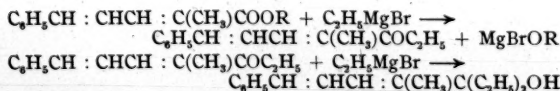
The high-melting ketone reacts with phenylmagnesium bromide in the cold to give a quantitative yield of tertiary alcohol. The low-melting ketone, on the other hand, does not

react with this reagent even on long boiling in ether solution. Its configuration, therefore, is such as to prevent the reaction with phenylmagnesium bromide. Although the ketones are undoubtedly optical isomers, their configuration must, then, be to a certain extent fixed, either as in the case of the symmetrically disubstituted succinic acids¹ or as a result of restricted rotation at the ethylene linkage.

With benzylmagnesium bromide the first reaction consists in replacement of the alkoxyl group of the methyl α -methylcinnamylidenacetate by the benzyl group; from this intermediate ketone two products are formed, one a ketone by addition of benzylmagnesium bromide in the 1,4 position, the other a tertiary alcohol by addition of the reagent in the 1,2 position. From this alcohol a hydrocarbon results by spontaneous loss of one molecule of water:



With ethylmagnesium bromide the only primary product isolated was a tertiary alcohol formed in accordance with the following equation:



The results of the investigation with methyl α -methylcinnamylidenacetate and with the other esters of the series are given in the following table and for comparison the results with benzylidene compounds are added. Since in the experiments with cinnamylidene esters secondary reactions interfered to a great extent with the separation of the primary products, the yields obtained are not quantitative:

¹ Ber. d. chem. Ges., 21, 3166; 24, 1876.

Structure	Magnesium compound	Per cent. of product formed by 1,4 addition	Per cent. of product formed by replacement of OR and 1,4 addition	Per cent. of product formed by replacement of OR and 1,2 addition
$^1\text{C}_6\text{H}_5\text{CH} : \text{CHCH} : \text{C} \begin{matrix} \text{COOR} \\ \text{CN} \end{matrix}$	$\text{C}_6\text{H}_5\text{MgBr}$	100		
$^2\text{C}_6\text{H}_5\text{CH} : \text{CHCH} : \text{C} \begin{matrix} \text{COOR} \\ \text{COOR} \end{matrix}$	$\text{C}_6\text{H}_5\text{MgBr}$	100		
$^3\text{C}_6\text{H}_5\text{CH} : \text{CHCH} : \text{C} \begin{matrix} \text{COOR} \\ \text{C}_6\text{H}_5 \end{matrix}$	$\text{C}_6\text{H}_5\text{MgBr}$	95		
$^4\text{C}_6\text{H}_5\text{CH} : \text{CHCH} : \text{C} \begin{matrix} \text{COOR} \\ \text{H} \end{matrix}$	CH_3MgI	76	87	100
$^5\text{C}_6\text{H}_5\text{CH} : \text{CHCH} : \text{C} \begin{matrix} \text{COOR} \\ \text{CH}_3 \end{matrix}$	$\text{C}_6\text{H}_5\text{MgBr}$		79	55
	$\text{C}_6\text{H}_5\text{MgBr}$			
	$\text{C}_6\text{H}_5\text{MgBr}$		100	30

¹ Macleod: *This Journal*, **44**, 331.² Reimer: *Ibid.*, **38**, 227.³ Reimer and Reynolds: *Ibid.*, **40**, 428.⁴ Reynolds: *Ibid.*, **44**, 198.⁵ This paper.

		Per cent. of product formed by addition of OR and 1.4 addition	Per cent. of product formed by addition of OR and 1.2 addition
¹ C ₆ H ₅ CH: C $\begin{smallmatrix} \text{COOR} \\ \text{CN} \end{smallmatrix}$	Magnesium compound C ₆ H ₅ MgBr	100	
² C ₆ H ₅ CH: C $\begin{smallmatrix} \text{COOR} \\ \text{COOR} \end{smallmatrix}$	CH ₃ MgI	100	
³ C ₆ H ₅ CH: C $\begin{smallmatrix} \text{COOR} \\ \text{C}_6\text{H}_5 \end{smallmatrix}$	C ₆ H ₅ MgBr	100	
⁴ C ₆ H ₅ CH: C $\begin{smallmatrix} \text{COOR} \\ \text{H} \end{smallmatrix}$	CH ₃ MgI	100	
⁵ C ₆ H ₅ CH: C $\begin{smallmatrix} \text{COOR} \\ \text{CH}_3 \end{smallmatrix}$	C ₆ H ₅ MgBr	50	100
	CH ₃ MgI	4	96
	C ₆ H ₅ MgBr		100
	CH ₃ MgI		

¹ Kohler and Reimer: THIS JOURNAL, **33**, 333.

² Kohler: *Ibid.*, **34**, 132.

³ Kohler and Heritage: *Ibid.*, **33**, 153.

⁴ Kohler and Heritage: *Ibid.*, **33**, 21.

⁵ Kohler: *Ibid.*, **36**, 529.

It will be seen that the course of the reaction with esters that have a strongly positive or a strongly negative α -substituent is the same in both series. The reactions which differ in the two series are those with esters having a phenyl group or a hydrogen atom in the α position. In a previous paper¹ this anomalous behavior of methyl α -phenylcinnamylidenacetate was attributed to the spatial configuration of the ester. Subsequent work² with the isomeric esters of cinnamylidenacetic acid, however, did not bear out that explanation. No conclusion as to the cause of the difference in behavior of the α -phenyl and α -hydrogen esters in the two series can be reached until other isomeric cinnamylidene esters have been prepared and investigated.

EXPERIMENTAL

The α -methylcinnamylidenacetic acid used in this work was first prepared by Perkin's synthesis.³ Later experiments showed that the tedious preparation of propionic anhydride might be avoided by heating at 160° for six hours a mixture of cinnamic aldehyde, propionyl chloride, and a large excess of sodium propionate. A 60 per cent. yield of acid was obtained by this method.

The methyl ester was prepared by boiling the acid in a 3 per cent. solution of hydrochloric acid in methyl alcohol for one hour. On cooling the ester separated from the solution in long, firm, colorless needles melting at 91°.

Reaction with Phenylmagnesium Bromide

In the first experiment two molecules of magnesium compound to one of the ester were used and the reaction carried out in cold, ethereal solution. When about one-half of the ester had reacted, a thick paste separated from the ether and any ester added after this point was recovered unchanged. It was found necessary to use at least four molecules of phenylmagnesium bromide to one of ester to avoid the separation of this pasty substance. After decomposition in the usual

¹ THIS JOURNAL, 40, 430.

² *Ibid.*, 40, 199.

³ J. Chem. Soc., 31, 406.

way, the product was boiled for one hour with dilute alcoholic potash to saponify any traces of ester that might have escaped reaction. After removal of the alcohol, the residue was extracted with water and the portion insoluble in water was distilled with steam to remove a considerable quantity of diphenyl. The residue was extracted with ether, the solution dried over calcium chloride, and the ester allowed to evaporate spontaneously. The product was a heavy, red oil from which there slowly separated a small quantity of needlelike crystals. These were filtered by suction and purified by repeated crystallization from methyl alcohol. The substance was found to be a ketone melting at 112° . A 17 per cent. yield was obtained. The oil was carefully fractionated under diminished pressure; there was some slight decomposition but most of the distillate boiled at 268° (10 mm.). Analyses of the oil gave the following results:

I. 0.1877 gram substance gave 0.6039 gram CO_2 and 0.1141 gram H_2O .

II. 0.1535 gram substance gave 0.4937 gram CO_2 and 0.0909 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{22}\text{O}$	I	Found II
C	88.34	87.74	87.71
H	6.74	6.76	6.57

These analyses indicated that the oil was a mixture of isomeric ketones but no separation was effected.

The reaction was repeated but no larger yield of crystalline product could be obtained by this method. The experiment was then carried out with six molecules of magnesium compound for one of the ester. Instead of boiling the product with alcoholic potash, as in the previous reactions, it was treated with a cold dilute solution of that reagent. From 20 grams of ester 5 grams of the 112° ketone were obtained, a 16 per cent. yield. The oily residue, on treatment with cold methyl alcohol, gradually deposited 10 grams of a ketone, isomeric with the first, which melted at 85° . This was found to isomerize to the higher-melting ketone on boiling its alcoholic solution with hydrochloric acid or potassium hydroxide. The

treatment of the product in the first experiments with boiling alcoholic potash had undoubtedly isomerized the low-melting ketone, at least partially, to the high-melting one, giving an oily mixture exceedingly difficult to separate. Accordingly, the experiment was repeated, omitting the treatment with alcoholic potash. The product was poured, in small quantities at a time, into cold methyl alcohol and the solid which separated was rapidly filtered with suction. It consisted almost entirely of low-melting ketone with only a trace of the high-melting isomer. The alcoholic filtrates deposited several grams of the oily product; the yield of the two solid ketones and the mixture was quantitative.

The amounts of the two ketones and of the oil varied greatly in different experiments so that it is impossible to give the relative quantities of each formed in the reaction. Attempts were made to determine the proportion of the two solid ketones by oxidation of the crude product of the Grignard reaction. This method was unsuccessful because benzoic acid was the only substance which could be isolated. Both ketones are soluble in methyl alcohol, the only solvent which could be used to affect their separation from the oil, and both dissolve readily in the oil itself. By careful manipulation of the mixture it was possible to separate, from time to time, small quantities of both ketones but nothing like a complete separation was ever accomplished. If this mixture was boiled with alcoholic potash, however, a considerable quantity of the high-melting ketone could be obtained; this method of procedure was subsequently adopted for the preparation of the quantities of this substance needed.

α-Methyl-β-phenyl-γ-benzalbutyrophenone (112°),

$C_6H_5CH : CHCH(C_6H_5)CH(CH_2)COC_6H_5$.—The substance separates from boiling methyl alcohol in bunches of stiff, white needles. It is readily soluble in chloroform, acetone, benzene and ether, slightly soluble in ligroin and warm alcohol. It dissolves in concentrated sulphuric acid to give a brilliant orange solution.

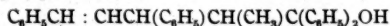
Analysis:

I. 0.1643 gram substance gave 0.5283 gram CO_2 and 0.0963 gram H_2O .

II. 0.1792 gram substance gave 0.5772 gram CO_2 and 0.1094 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{22}\text{O}$	I	Found
C	88.34	88.00	87.90
H	6.74	6.39	6.78

Reaction with Phenylmagnesium Bromide. 2-Methyl-1,1,3,5-tetraphenyl-4-pentene-1-ol,



—Four grams of ketone were dissolved in absolute ether and added to a solution of 6 grams of phenylmagnesium bromide cooled to 0° . A reaction took place at once, the magnesium compound separating as a white crystalline solid. The product was decomposed as usual; the ethereal solution deposited, on evaporation, a white solid which, after repeated crystallizations from hot methyl alcohol, separated in clear prisms which softened at 132° and melted at 150° . It was heated at 110° to free it of alcohol of crystallization and analyzed.

Analysis:

0.1465 gram substance gave 0.4796 gram CO_2 and 0.0932 gram H_2O .

	Calculated for $\text{C}_{30}\text{H}_{32}\text{O}$	Found
C	89.10	89.27
H	6.93	7.06

The compound is very soluble in ether, acetone, benzene, chloroform and boiling methyl and ethyl alcohols, slightly soluble in ligroin. It was proved to be a tertiary alcohol by treatment with ethylmagnesium bromide. A gas was evolved and after decomposition of the Grignard product the original substance was recovered unchanged.

The structure of the tertiary alcohol was established by oxidation. An acetone solution of 3.8 grams of the solid was treated at room temperature with finely powdered potassium permanganate as long as decolorization took place. The oxides of manganese were then separated by filtering with suction and the acetone allowed to evaporate spontaneously. The solid, deposited on complete removal of the solvent, was

washed with cold methyl alcohol; 1.5 grams were obtained melting at 187°. Extraction of the oxides of manganese with boiling water gave a solution from which 0.5 gram of benzoic acid was precipitated. Finally the solution of the oxides of manganese in sulphuric acid, to which sulphur dioxide had been added, was extracted with ether. On evaporation of the ether, a mixture was left which was separated by treatment with cold methyl alcohol, 0.3 gram of benzoic acid dissolving in the methyl alcohol and 0.5 gram of the 187° solid remaining undissolved. This solid is very soluble in chloroform and acetone, only very slightly soluble in ether and methyl alcohol. It crystallizes in fine white needles from acetone, from a mixture of chloroform and methyl alcohol and from absolute alcohol.

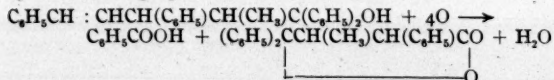
Analysis:

0.1528 gram substance gave 0.4720 gram CO₂ and 0.0830 gram H₂O.

	Calculated for C ₂₂ H ₂₀ O ₂	Found
C	84.14	84.24
H	6.09	6.03

The substance is the lactone of *γ*-hydroxytriphenylmethylbutyric acid, formed by loss of one molecule of water from the *γ*-hydroxy acid which is a primary product of the reaction. It is insoluble in hot sodium carbonate and only very slightly soluble in aqueous potassium hydroxide. It dissolves readily, however, in potassium hydroxide to which a small amount of alcohol has been added. On evaporation of the alcohol and acidification of the ice-cold aqueous solution, the lactone is recovered unchanged.

The oxidation of the tertiary alcohol may be represented by the following equation



Reaction with Bromine. Dibromo-*α*-methyl-*β*-phenyl-*γ*-benzalbutyrophene, C₆H₅CHBrCHBrCH(C₆H₅)CH(CH₃)COC₆H₅.—Two grams of *α*-methyl-*β*-phenyl-*γ*-benzalbutyrophene (112°)

were dissolved in chloroform and the solution cooled with ice. To this was added, drop by drop, a solution of one gram of bromine in chloroform. The solution was instantly decolorized. After standing for one hour the chloroform was allowed to evaporate spontaneously. The pasty product was dissolved in the smallest possible quantity of cold chloroform and twice the volume of methyl alcohol added. Fine, white needles separated rapidly; after several crystallizations, the substance melted with decomposition at 180° . The analysis shows the compound to be the dibromo addition product of the ketone.

Analysis:

0.1550 gram substance gave 0.3369 gram CO_2 and 0.0646 gram H_2O .

	Calculated for $\text{C}_{24}\text{H}_{22}\text{OBr}_2$	Found
C	59.25	59.27
H	4.52	4.63

The substance is very readily soluble in ether, chloroform, acetone and benzene, very slightly soluble in boiling alcohol.

The filtrate from which this bromine compound separated left, on evaporation, an oil and also a small quantity of a second crystalline compound. Repeated attempts to accumulate enough of this crystalline substance for analysis were unsuccessful. It separates from alcohol in soft, branching needles, melting at 115° and decomposing at about 180° . It was at first thought that this compound was a monobromide, formed by loss of hydrobromic acid from the dibromide, but as the latter substance could not be made to lose a molecule of hydrobromic acid under the most rigorous treatment, it is probable that the low-melting compound is an isomeric dibromo addition product of the ketone.

Oxidation of the Ketone (112°).—An acetone solution of the ketone was treated with powdered potassium permanganate; the reaction was so very slow that at the end of six hours a portion of the 2.3 grams of ketone used was not oxidized. The solution was filtered with suction and the acetone allowed to evaporate spontaneously; a very small amount of resinous

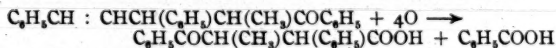
material was left and also 0.6 gram of unchanged ketone. The oxides of manganese were extracted several times with boiling water. A mixture of two acids separated on acidifying the aqueous solution. The mixture was separated, though not completely, by taking advantage of the difference in solubility of the two acids in ligroin. By careful extraction with boiling ligroin benzoic acid was removed, and the portion left undissolved was purified by recrystallization from a mixture of chloroform and ligroin; it separates in fine white needles melting at 131° , is very soluble in chloroform, ether, methyl and ethyl alcohols, less soluble in ligroin and cold water.

Analysis:

0.1282 gram substance gave 0.3563 gram CO_2 and 0.0688 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{16}\text{O}_3$	Found
C	76.11	75.80
H	5.97	5.96

The substance is *methylphenylbenzoylpropionic acid*. Its formation may be represented by the following equation:



Methyl Methylphenylbenzoylpropionate,

$\text{C}_6\text{H}_5\text{COCH}(\text{CH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{COOCH}_3$.—The ester was prepared by treating 1.3 grams of acid with a saturated solution of hydrochloric acid in methyl alcohol. After standing overnight one gram of solid product separated; this was washed with cold methyl alcohol and crystallized from the same solvent. The ester separates in heavy plates melting at 105° ; it is very soluble in chloroform, acetone, ether and warm methyl alcohol, very slightly soluble in ligroin.

Analysis:

0.1500 gram substance gave 0.4177 gram CO_2 and 0.0845 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{18}\text{O}_3$	Found
C	76.59	75.94
H	6.38	6.26

A very small quantity of another ester, melting at 87° , was separated on complete evaporation of the solution but sufficient material was not obtained for analysis.

α -Methyl- β -phenyl- γ -benzalbutyrophenone (85°), $C_6H_5CH : CHCH(C_6H_5)CH(CH_3)COC_6H_5$.—This substance crystallizes from alcohol in stiff, white needles. It is very soluble in chloroform, ether, absolute alcohol, methyl alcohol, benzene and acetone, less soluble in ligroin. It dissolves in concentrated sulphuric acid to give a reddish yellow solution. It may be separated from its high-melting isomer by extracting the mixture repeatedly with cold absolute alcohol; from the solution it separates in thick needles melting at 85° .

Analysis:

I. 0.1416 gram substance gave 0.4560 gram CO_2 and 0.0860 gram H_2O .

II. 0.1622 gram substance gave 0.5233 gram CO_2 and 0.0985 gram H_2O .

	Calculated for $C_{24}H_{20}O$	Found	
		I	II
C	88.34	87.80	87.98
H	6.74	6.74	6.74

A solution of this ketone in methyl alcohol containing dry hydrochloric acid was boiled for four hours. The solid which crystallized from the solution was almost pure high-melting ketone. This same isomerization was carried out by boiling the ketone or the oily mixture of ketones with potassium hydroxide in alcoholic solution. In this reaction there was always a residue which could not be made to solidify.

Reaction with Phenylmagnesium Bromide.—One and three-tenths grams of ketone, in ether solution, were treated with phenylmagnesium bromide cooled in ice water. The ethereal solution, obtained in the usual way, was allowed to evaporate spontaneously. The whole amount of ketone was recovered unchanged. The substances were then brought together in boiling ethereal solution and the mixture boiled for one hour. The ketone was again recovered unchanged.

Reaction with Bromine.—Seven-tenths of a gram of the ketone was dissolved in chloroform, the solution cooled to 0°

and 0.35 gram of bromine in chloroform added. Decolorization of the bromine took place at once. After the solvent had evaporated, the oily product remaining was dissolved in the least possible quantity of chloroform and twice the volume of methyl alcohol added. A small quantity of crystalline compound, melting with decomposition at 180° , was formed; it was found to be identical with the dibromo addition product of the high-melting ketone. From the yellowish oil, left after complete evaporation of the filtrate, no solid substance could be separated.

Since the isomerism of the ketones has been proved to be optical, the formation of this compound is evidently due to the isomerization of the low-melting to the high-melting ketone, under the influence of bromine or of a small quantity of hydrobromic acid formed in the reaction, and the formation from this of the dibromo compound already described.

Oxidation of the Ketone (85°).—The ketone was dissolved in acetone and treated with powdered potassium permanganate; decolorization took place rapidly and oxidation of 2 grams was complete in two hours. The solution was filtered at once and the oxides of manganese were repeatedly extracted with small quantities of boiling water. On acidifying the cold aqueous solution, an oily substance which solidified at once in contact with ligroin was precipitated. This product was a mixture of two acids which were completely separated by several extractions with boiling ligroin; the ligroin solution contained the entire yield of benzoic acid and a white solid remained undissolved. This insoluble acid was purified by recrystallization from a mixture of chloroform and ligroin, from which it separates in fine white needles melting at 145° . It is very soluble in chloroform, ether, benzene, methyl and ethyl alcohols, almost insoluble in ligroin and cold water.

Analysis:

0.1526 gram substance gave 0.4248 gram CO_2 and 0.0793 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{16}\text{O}_3$	Found
C	76.11	75.92
H	5.97	5.77

The acid is *methylphenylbenzoylpropionic acid*, isomeric with the oxidation product obtained from the 112° ketone.

An ester was prepared by treating 1.3 grams of acid with a saturated solution of hydrochloric acid in methyl alcohol. On standing overnight, a quantitative yield of ester, melting at 105°, identical with that from the isomeric acid, separated from the solution. It is probable, therefore, that the low-melting ester, obtained only from the 131° acid, is the derivative of that acid and that the small yield of this ester and the large yield of the 105° ester obtained from the 131° acid may be due to the isomerization of that acid to the high-melting isomer under the influence of hydrochloric acid. This conclusion is borne out by the fact that on saponification of the 87° ester a mixture of the two acids results.

Reaction with Benzylmagnesium Bromide

An ethereal solution of 7 grams of methyl α -methylcinnamylidenacetate was allowed to react with a large excess of benzylmagnesium bromide. After a half hour the product was decomposed with iced hydrochloric acid, the solution extracted with ether, the ether evaporated, and the remaining yellow liquid distilled with steam until the dibenzyl was completely removed. The yellow product was extracted with ether and the ethereal extract dried. On evaporation of the solvent, 3.5 grams of solid separated. This was washed carefully with methyl alcohol and recrystallized from a mixture of chloroform and methyl alcohol, from which it separates in clusters of iridescent needles melting at 117°. It is very soluble in chloroform, less soluble in ligroin, ether and acetone, and only very slightly soluble in methyl and ethyl alcohols.

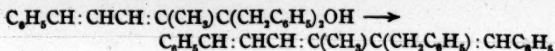
Analysis:

0.1590 gram substance gave 0.5395 gram CO₂ and 0.0995 gram H₂O.

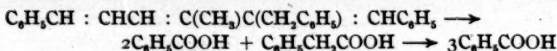
	Calculated for C ₂₀ H ₂₄	Found
C	92.85	92.53
H	7.14	6.95

The substance is *methylphenylbenzylbenzal-1,3-pentadiene*,

formed by loss of one molecule of water from α, α -dibenzyl- β -methyl- δ -benzalcrotonyl alcohol:



The structure of the hydrocarbon was established by oxidation. An acetone solution of 5 grams of the solid, cooled with ice water, was treated with finely powdered potassium permanganate until it was no longer decolorized. The solution was filtered and the acetone allowed to evaporate; no residue was left after complete removal of the solvent. The oxides of manganese were then extracted with boiling water; 2.7 grams of benzoic acid were precipitated from the aqueous solution. Also 2.4 grams of benzoic acid were obtained by dissolving the oxides in sulphuric acid, to which sulphur dioxide had been added, and extracting the solution with ether. The only other product of oxidation was a trace of phenylacetic acid. The reaction may be represented as follows:



Since complete oxidation of 5 grams of hydrocarbon should give 5.4 grams of benzoic acid, a yield of 5.1 grams of this acid indicates that the phenylacetic acid, which was first formed in the reaction, was subsequently almost entirely oxidized to form a third molecule of benzoic acid.

The product from the Grignard reaction which was not solid was heated for three hours with acetic anhydride in order that any α, α -dibenzyl- β -methyl- δ -benzalcrotonyl alcohol present might be decomposed. When the liquid was poured into water no hydrocarbon separated. Accordingly the yellow liquid was extracted with ether and the ethereal extract washed and dried over calcium chloride. After evaporation of the ether, the residue was distilled under diminished pressure; 8 grams of viscous, yellow liquid distilled at 265° (20 mm.).

Analysis:

0.1600 gram substance gave 0.5150 gram CO_2 and 0.0975 gram H_2O .

	Calculated for $C_{26}H_{26}O$	Found
C	88.13	87.88
H	7.34	6.77

The substance is α -methyl- β -benzyl- γ -benzalpropyl benzyl ketone, $C_6H_5CH:CHCH(CH_2C_6H_5)CH(CH_2)COCH_2C_6H_5$. When treated with ethylmagnesium bromide no gas was evolved; moreover, the ketone does not react with ethylmagnesium bromide, the original substance being recovered on decomposition of the Grignard product. This behavior indicates that the configuration of this ketone may be like that of the low-melting solid obtained in the reaction with phenylmagnesium bromide.

The ketone reacts readily with bromine, but a solid could not be separated from the dark brown product obtained.

The yield of ketone in the Grignard reaction with benzylmagnesium bromide was 65 per cent. and the yield of hydrocarbon 30 per cent.

Reaction with Ethylmagnesium Bromide

An ethereal solution of methyl α -methylcinnamylidenacetate was added slowly to a large excess of ethylmagnesium bromide until an oily layer began to separate from the ether. The reaction was then stopped and the Grignard product decomposed at once with iced hydrochloric acid; the solution was extracted with ether, the ethereal extract washed and dried over calcium chloride. The yellow liquid, left after removal of the ether, was distilled under diminished pressure. Its behavior indicated that it was a mixture, which apparently was not separated by distillation. Analyses of various fractions confirmed this assumption. Accordingly, the reaction was repeated and the product treated with cold aqueous potash and allowed to stand for a day. The alcohol was then evaporated in a current of air and the residue extracted with cold water. A small quantity of acid was precipitated from the aqueous solution. The portion insoluble in water was extracted with ether and the liquid, obtained after evaporation of the ether, was distilled under diminished pressure. This, likewise, did not behave like a pure substance and analyses of several fractions again indicated a mixture.

The procedure next adopted was to saponify the crude product by boiling with alcoholic potash. The alcohol was removed and the aqueous solution, obtained by extracting the residue with water, deposited, on acidification, several grams of acid. From the portion insoluble in water a lemon-yellow mobile liquid was separated which distilled constantly at 200° (20 mm.); 14.5 grams resulted from 43 grams of ester. Yield, 30 per cent.

Analysis:

0.1654 gram substance gave 0.5067 gram CO_2 and 0.01272 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{20}\text{O}$	Found
C	83.47	83.54
H	9.56	8.54

The substance is α, α -diethyl- β -methyl- δ -benzalcrotonyl alcohol, $\text{C}_6\text{H}_5\text{CH}:\text{CHCH}:\text{C}(\text{CH}_3)\text{C}(\text{C}_2\text{H}_5)_2\text{OH}$. It was proved to be a hydroxyl compound by treatment with ethylmagnesium bromide. A gas was evolved and the original tertiary alcohol was recovered on decomposition of the Grignard product.

A high-boiling, viscous liquid, which distilled persistently with decomposition, was also separated by distillation under diminished pressure. On long standing this deposited an ester, melting at 185° , which was purified by crystallization from a mixture of ether and chloroform. Analyses indicated that it was not a primary product of the reaction.¹

By saponification of the crude Grignard product from 43 grams of cinnamylidene ester, 12 grams of crude, yellow acid were obtained. This partially liquefied in the air and was very difficult to purify. About one gram of acid melting at 207° was finally separated pure by use of ligroin and methyl alcohol as solvents. Analyses, likewise, showed that this acid is not a primary product of the Grignard reaction. Neither this nor the ester were investigated further.

Since the corresponding tertiary alcohol obtained in the reaction with ethylmagnesium bromide and methylcinnamylidenacetate was almost completely decomposed by boiling with alcoholic potash,² it is possible that the course of pro-

¹ Cf. THIS JOURNAL, 34, 568; 40, 198.

² *Ibid.*, 40, 211.

cedure adopted in order to separate the α, α -diethyl- β -methyl- δ -benzalcrotonyl alcohol from the other products of the Grignard reaction may account for the small yield of tertiary alcohol separated.

CHEMICAL LABORATORY
BARNARD COLLEGE
May, 1912

ACTION OF HEAT ON *p*-SULPHAMIDO-*o*-TOLUIC ACID

BY JOHN W. NOWELL

The work of Hartman, Muckenfuss, Stoddard, Chamberlain, Simmons and Rouiller¹ has shown that in the peculiar change undergone by *p*-sulphamidobenzoic acid when it is heated several hours at 220° one of the resulting products is *p*-sulphobenzamidine, $\text{HO}_3\text{SC}_6\text{H}_4\text{C}(\text{:NH})\text{NH}_2$, or its inner salt. Nakaseko² found that *m*-sulphamidobenzoic acid, in which the sulphonic and carboxylic groups are in the meta instead of the para position to each other, gives an analogous product, and Chamberlain³ likewise showed this to be true of *p*-sulphamido-*m*-toluic acid, in which the meta position to the carboxyl is occupied by a methyl group. Inasmuch as *o*-substituted amidines cannot be obtained by the Pinner method and Rouiller found no indication of the formation of such a compound by his method when applied to *o*-nitrobenzoic acid, although the *m*- and *p*-acids reacted smoothly,⁴ it became of interest to determine whether substituents in the ortho position to the carboxylic group in *p*-sulphamidobenzoic acid would prevent the formation of an amidine. In the one case studied, viz., that of *p*-sulphamido-*o*-toluic acid, such was found to be the case; the only products obtained were

¹ For a summary of this work, see THIS JOURNAL, 47, 475.

² *Ibid.*, 47, 429.

³ *Ibid.*, 47, 333.

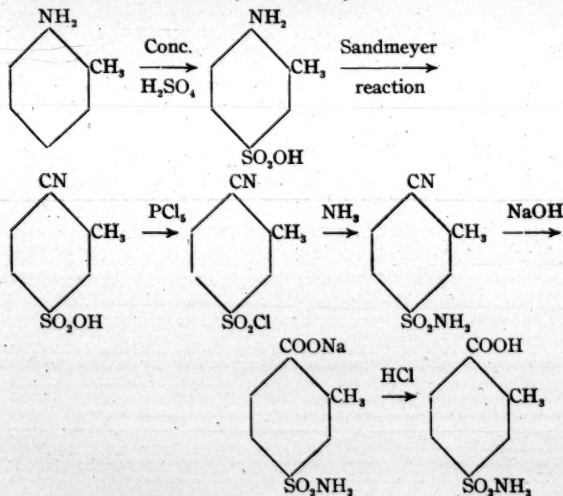
⁴ *Ibid.*, 47, 490. In the case of the *o*-acid, no attempt was made to isolate an amidine, as the product, on distillation with magnesium and sodium hydroxides, successively, lost, as ammonia, 61.3 per cent. of the nitrogen originally present as benzenesulphonamide with the magnesium hydroxide, and only 3.5 per cent. with the sodium hydroxide, whereas any amidine, if formed, should lose equal amounts of nitrogen with each reagent. It was concluded, therefore, that practically nothing but an ammonium salt was formed. It may be, however, that the nitro group in the *o*-position prevented the hydrolysis of any amidine which might have been formed. The experiment will be repeated on a larger scale and an attempt made to isolate all the products formed.—C. A. R.

acid ammonium *p*-sulpho-*o*-toluate and carbamido-*o*-toluene-*p*-sulphonic acid. Rouiller has shown that carboxamides are probably intermediate products in the formation of amidines from carboxylic acids and sulphonamides,¹ and it therefore appears that the effect of the *o*-methyl group has been to arrest the reaction at this intermediate stage.

Attempts were made to prepare other *o*-substituted *p*-sulphamidobenzoic acids, but the difficulties encountered were so great that this could not be done in the time at the author's disposal.

Preparation of Material

On looking into the literature, it was found that Jacobsen² had prepared *p*-sulphamido-*o*-toluic acid by oxidizing *p*-sulphamido-*o*-xylene, but in view of the fact that *o*-xylene is rather costly and difficult to obtain in sufficient quantities, the following method for preparing *p*-sulphamido-*o*-toluic acid was tried and found to be very satisfactory:



¹ THIS JOURNAL, 47, 486.

² Ber. d. chem. Ges., 11, 22; 14, 39.

p-Sulpho-*o*-toluidine, prepared according to the directions of Neville and Winther,¹ was diazotized in the usual manner. The diazotized product precipitated out of solution so I filtered it off and added it, suspended in water, to the cuprous cyanide solution. When the solution had cooled, I added hydrochloric acid and a dirty, yellowish gray precipitate came down, consisting chiefly of copper salts. This clayey looking precipitate was filtered off and the solution concentrated to about one-third its volume. On cooling, the potassium salt of *p*-sulpho-*o*-tolunitrile crystallized out in long silky needles and from more concentrated solutions in rosettes with needles radiating from the center. The last portions were extracted with boiling alcohol to separate the nitrile from inorganic salts. Yield, about 90 per cent. of the theoretical.

Preparation of the Chloride of p-Sulpho-o-tolunitrile.—The above potassium salt was treated with its own weight of phosphorus pentachloride (slightly more than one molecule), and rubbed up in a mortar, when a vigorous reaction took place and the whole mass melted to a thick, brownish yellow liquid. The product was heated for some time on the water bath to drive off all fumes and to complete the reaction. When cool, it was washed with ice water, generally about six or seven times, to take out all inorganic salts. The product crystallized from ligroin in beautiful, colorless crystals, mostly diamond-shaped or rather elongated diamonds with striations on the faces, melting at 52°.5–53°. Yield, about 50 per cent.

Preparation of p-Sulphamido-o-tolunitrile.—The crude acid chloride, after being washed about six times with ice water, was treated with concentrated ammonia. When stirred vigorously, a very noticeable reaction set in and in a short time all the acid chloride dissolved, leaving a clear, brownish yellow solution. On concentrating to a small volume, which eliminated the excess of ammonia, the *p*-sulphamido-*o*-tolunitrile came down in brownish fluffy crystals which, after boiling with charcoal, separated in long crystals with rough edges somewhat like saw teeth. After several recrystalliza-

¹ Ber. d. chem. Ges., 13, 1940.

tions, the crystals still had a slight yellowish color but the melting point was constant at 159° – 160° . Yield, about 75 per cent.

Preparation of p-Sulphamido-o-toluic Acid.—The *p*-sulphamido-*o*-tolunitrile was digested for six hours with an excess of caustic soda. There was a copious evolution of ammonia. When the reaction was complete, the solution was cooled and acidified with hydrochloric acid, when the whole mass almost solidified, so fine and silky were the crystals. After five crystallizations, the acid came out in beautiful colorless, silky needles, melting at 211° . From five hundred grams of *o*-toluidine I obtained one hundred and fifty grams of the crystallized acid.

Analyses:

0.3643 gram heated two hours at 109° lost 0.0004 gram.

0.3643 gram heated two hours at 150° gained 0.0013 gram.

0.5057 gram heated two hours at 145° gained 0.0001 gram.

From the above results it is evident that *p*-sulphamido-*o*-toluic acid contains no water of crystallization.

0.6066 gram of the acid required 28.25 cc. of 0.1 N alkali to neutralize it.

0.5741 gram of the acid required 26.72 cc. of 0.1 N alkali to neutralize it.

	Calculated for $\text{CH}_3\text{C}_6\text{H}_3(\text{SO}_2\text{NH}_2)\text{COOH}$	I	Found	II
Molecular weight	215.15	214.72	214.85	

0.1994 gram gave 0.2105 gram BaSO_4 (Liebig).

0.2270 gram gave 0.2485 gram BaSO_4 (Liebig).

	Calculated for $\text{CH}_3\text{C}_6\text{H}_3(\text{SO}_2\text{NH}_2)\text{COOH}$	I	Found	II
S	14.9	14.5	15.03	

Potassium Salt.—This salt was prepared by neutralizing 5 grams of *p*-sulphamido-*o*-toluic acid with potassium hydroxide and evaporating to crystallization, when it came out in beautiful colorless, glasslike crystals. It has been described by Jacobsen¹ as glassy prisms of rhombohedral habit.

Analyses:

0.6362 gram lost 0.0222 gram of water at 150° .

¹ Ber. d. chem. Ges., 14, 39.

- 0.6002 gram lost 0.0207 gram of water at 150°.
 0.6140 gram gave 0.2057 gram K_2SO_4 .
 0.5795 gram gave 0.1938 gram K_2SO_4 .

Calculated for $CH_3C_6H_3(SO_2NH_2)COOK + 0.5H_2O$		I	Found	II
K	14.89	15.03		15.00
H ₂ O	3.43	3.44		3.48

Ammonium Salt.—By treating *p*-sulphamido-*o*-toluic acid with ammonia, a substance was obtained which crystallized easily from concentrated water solutions in crystals like elongated diamonds melting at 169°–172°. In no case was the melting point sharp at all.

0.4224 gram gave with $Mg(OH)_2$ ammonia equivalent to 16.9 cc. 0.1 cc. 0.1 N acid.

0.5246 gram lost 0.041 gram at 120°

Calculated for $CH_3C_6H_3(SO_2NH_2)COONH \cdot H_2O$		Found
0.5 N	5.60	5.60
H ₂ O	7.20	7.81

Preparation of Acid Ammonium *p*-Sulpho-*o*-toluate.—Following Waters' method¹ for preparing his acid ammonium salt, ten grams of *p*-sulphamido-*o*-toluic acid were mixed in a sealed tube with 20 cc. of concentrated hydrochloric acid and heated at 200° for ten hours. On removal of the tube from the furnace, small prismatic crystals were observed all through the mass. The contents of the tube were dissolved in water and on concentrating the solution, prismatic crystals melting at 285°–288° were obtained. After about six crystallizations from water, I obtained crystals having a melting point of 288°–289°. The salt was identical with that obtained by heating the sulphamido acid at 220° (see p. 238).

Attempt to Prepare the Diammonium Salt of *p*-Sulpho-*o*-toluic Acid.—I hydrolyzed potassium *p*-sulpho-*o*-tolunitrile with caustic potash, then saturated an alcoholic solution of the resulting salt with hydrochloric acid gas, when the potassium chloride was precipitated out and the filtered solution evaporated to dryness to remove the hydrochloric acid. The

¹ Diss., Johns Hopkins Univ., 1899, p. 28. THIS JOURNAL, 47, 349.

free *p*-sulpho-*o*-toluic acid was now neutralized with ammonia but I was never able to get the diammonium salt out pure enough for analysis, because it is hydrolyzed so easily. By recrystallizing from acetone, I obtained shiny grains melting at 211° – 215° . From water it came down as long, slender prisms at first, about half of which melted at 215° , and the remainder at 269° – 271° . On standing overnight the bottom of the beaker became covered with short, thick prisms, identical in appearance with the acid ammonium salt and which showed no signs of melting till 275° was reached. The solution had also become distinctly acid, proving conclusively that the diammonium salt was being hydrolyzed to the acid ammonium salt. No analysis was made, as crystals of a definite melting point were not obtained. See also page 237 for the analogous behavior of the solution of the product obtained by heating *p*-sulphamido-*o*-toluic acid and then neutralizing with ammonia.

Waters¹ encountered the same difficulty in trying to prepare the diammonium salt of *p*-sulpho-*m*-toluic acid by precipitating exactly the barium from a solution of the sulphotoluic acid by means of ammonium sulphate. Instead of obtaining the diammonium salt, he obtained only the acid ammonium salt. He says that "this surprising result could be due only to a loss of ammonia on evaporating the solution."

Preparation of the Acid Barium p-Sulpho-o-toluate.—Thirty grams of the product obtained by heating *p*-sulphamido-*o*-toluic acid (see page 236) were dissolved in water and divided into two equal parts. One part was just neutralized with barium hydroxide and then added to the other half of the solution. On standing overnight a grayish powder came down and, over it, some clusters of needles very soluble in water. When boiled with charcoal and recrystallized from water, the substance came out in small, shiny, silky plates which showed no signs of melting up to 300° . After several recrystallizations from water, I obtained pure white needles arranged mostly in rosettes which, when dried, had a leafy, glassy appearance.

¹ Diss., Johns Hopkins Univ., 1899, p. 28.

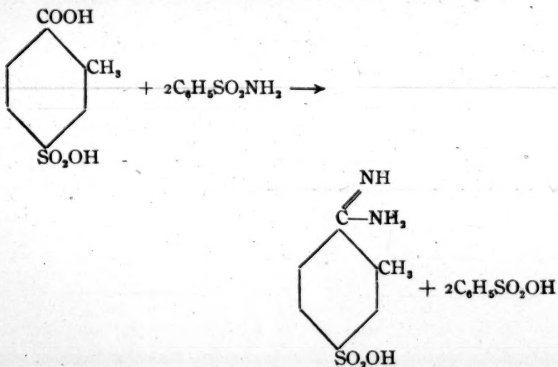
Analyses:

0.4188 gram gave 0.1635 gram BaSO₄ (Liebig).0.4256 gram gave 0.1653 gram BaSO₄ (Liebig).

0.3091 gram lost 0.0182 gram when heated 8 hours at 175°.

	Calculated for (CH ₃ C ₆ H ₃ COOH SO ₃) ₂ Ba.2H ₂ O	Found
Ba	22.77	22.85-22.97
H ₂ O	5.96	5.88

*Attempt to Prepare p-Sulpho-*o*-toluamidine.*—*p*-Sulpho-*o*-toluic acid was made by digesting *p*-sulpho-*o*-tolunitrile with an excess of barium hydroxide, till hydrolysis was complete, then the barium was exactly precipitated with sulphuric acid and the filtered solution evaporated to dryness, when the free sulphotoluic acid was obtained as a white amorphous powder. By heating *p*-sulpho-*o*-toluic acid with benzenesulphonamide, I hoped to obtain the amidine by the following reaction:



Twelve grams of the acid and eighteen grams of benzenesulphonamide were thoroughly mixed and heated in a sealed tube for two and one-half hours at 225°. The mixture melted to a dark brown mass which was readily soluble in cold water except for a trace of carbonaceous matter. The solution was

extracted three times with 25 cc. portions of ether and on evaporating the ether extract, there remained a few oily drops which had a distinct nitrile odor and gave off ammonia with sodium hydroxide. The water solution was just neutralized with barium hydroxide and evaporated to dryness. I then extracted the dry residue with absolute alcohol that I might separate the barium salts from the products soluble in alcohol.

Alcoholic Extract.—When evaporated to crystallization, the alcoholic solution deposited an amorphous powder melting at 245° – 275° . I was never able to get any characteristic crystals. After three recrystallizations, the substance melted at 270° – 290° and gave off about twice as much ammonia with magnesium hydroxide as with sodium hydroxide, though the amount of ammonia was far too small for the acid ammonium salt.

0.3405 gram gave with $\text{Mg}(\text{OH})_2$ ammonia equal to 2.7 cc. 0.1 N acid and with NaOH ammonia equal to 1.15 cc. 0.1 N acid.

	Calculated for	
	$\text{CH}_3\text{C}_6\text{H}_3\begin{cases} \text{COOH} \\ \text{SO}_2\text{NH}_4 \end{cases}$	
N	6.01	Found
		1.58

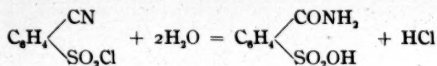
Substance Insoluble in Alcohol.—The portion insoluble in alcohol was treated with ammonium sulphate till the barium was just precipitated, the barium sulphate filtered off and the solution evaporated to dryness. The dried residue was then dissolved in alcohol and precipitated with ether, by which method I obtained an amorphous powder melting at 240° – 252° . The ammonia liberated from this substance by boiling 0.250 gram with magnesium hydroxide neutralized 18.6 cc. 0.1 N acid and that set free by caustic soda neutralized only 0.45 cc. 0.1 N acid, so it is evident that the nitrogen is present in the form of ammonium salts, very probably a mixture of $\text{C}_6\text{H}_3\text{SO}_2\text{NH}_4$ and $\text{CH}_3\text{C}_6\text{H}_3\begin{cases} \text{COONH}_4 \\ \text{SO}_2\text{ONH}_4 \end{cases}$. Not a trace of amidine was found.

Attempts to Prepare Carbamido-o-toluene-p-sulphonic Acid.—

The method of Radziszewski¹ for obtaining amides from nitriles by the action of hydrogen peroxide was first tried. Potassium *p*-sulpho-*o*-tolunitrile was treated with a slightly alkaline solution of hydrogen peroxide and warmed on the water bath at 40° till the evolution of gas ceased. On concentration, the solution deposited only an amorphous powder which, when treated with ammonia, gave a substance melting at 185°–195°, chiefly the diammonium salt of *p*-sulpho-*o*-toluic acid, showing that the nitrile group was saponified completely to the carboxyl group, yielding only *p*-sulpho-*o*-toluic acid.

Simmons² found the same thing in the case of *p*-sulphobenzonitrile, for when he treated the nitrile with alkaline hydrogen peroxide, he got only *p*-sulphobenzoic acid.

I next tried the method of Jesurun,³ who obtained *p*-sulphobenzamide by the following reaction:



the reaction taking place in a sealed tube at 95°–100°. Five grams of potassium *p*-sulpho-*o*-tolunitrile with 5 cc. of 0.1 N sulphuric acid were heated in a sealed tube for five hours at 100°. When the tube was opened and the contents evaporated to crystallization, I obtained the original nitrile unchanged.

The successful method for preparing the carbamido-*o*-toluene-*p*-sulphonic acid was finally discovered accidentally. All attempts to prepare the free sulphotolunitrile from the potassium salt by dissolving it in water and acidifying with hydrochloric acid having failed, I dissolved the salt in absolute alcohol and saturated the solution with dry hydrogen chloride gas, hoping thus to throw out the potassium as potassium chloride and obtain the free *p*-sulpho-*o*-tolunitrile. During the process the temperature was allowed to rise almost to the boiling point of the alcohol. The potassium chloride was filtered off and the alcoholic solution evaporated to a small volume but nothing would crystallize out, so I evaporated the

¹ Ber. d. chem. Ges., 18, 355.

² Diss., Johns Hopkins University, 1901.

³ Ber. d. chem. Ges., 22, 2289.

solution to dryness and heated the residues on the water bath till all the hydrochloric acid was expelled. The residue was strongly acid. It was neutralized with ammonia and on crystallization I obtained beautiful, long, prismatic crystals melting at 276° – 278° .

Analysis:

0.3081 gram gave with $\text{Mg}(\text{OH})_2$ ammonia equivalent to 13.1 cc. 0.1 N acid, and with NaOH ammonia equivalent to 13.6 cc. 0.1 N acid.

0.5 N	Calculated for		Found	
	$\text{CH}_3\text{C}_6\text{H}_5(\text{CN})\text{SO}_2\text{NH}_4$	$\text{CH}_3\text{C}_6\text{H}_5(\text{CONH}_2)\text{SO}_2\text{NH}_4$	$\text{Mg}(\text{OH})_2$	NaOH
	6.54	6.03	5.95	6.18

Preparation of the Barium Salt—Another portion of the acid residue was neutralized with barium hydroxide, and after several crystallizations I was able to get out the barium salt reasonably pure.

Analysis:

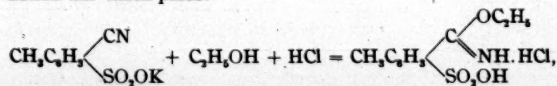
0.5183 gram lost 0.0283 gram at 200° .

0.6933 gram gave 0.2687 gram BaSO_4 .

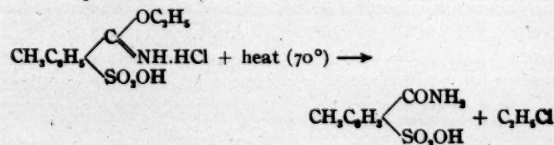
0.3224 gram gave 0.1250 gram BaSO_4 .

	Calculated for		Found	
	$[\text{CH}_3\text{C}_6\text{H}_5(\text{CONH}_2)\text{SO}_2]_2\text{Ba} \cdot 2\text{H}_2\text{O}$	I		II
Ba	22.84	22.80		22.81
H ₂ O	5.99	5.46		...

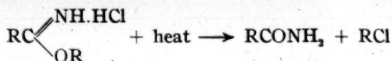
From the above analyses of the ammonium and barium salts of this acid it seems very probable that the following reaction has taken place:



and that the imido ester at the temperature of the reaction breaks up as follows:



Pinner¹ says that imido esters in the solid state break down as follows when heated:



so to satisfy myself that the same reaction takes place in alcohol when the temperature is allowed to rise nearly to the boiling point, I tested benzonitrile in the same way as the sulphotolunitrile above and though I obtained some ammonium chloride, I also was able to isolate quite a considerable amount of benzamide. The ammonium chloride, being insoluble in absolute alcohol, was filtered off and on concentrating the alcoholic solution a white crystalline substance came out having a melting point of 128°, identical with that of benzamide, and when mixed with benzamide the melting point remained constant. Judging from the analyses of the two salts and the analogous experiment with benzonitrile, it is pretty conclusively shown that by treating an alcoholic solution of potassium *p*-sulpho-*o*-tolunitrile with hydrochloric acid gas, there is formed, not *p*-sulpho-*o*-tolunitrile, but 1-carbamido-2-methylbenzene-4-sulphonic acid.

Determination of the Most Suitable Conditions for Heating p-Sulphamido-o-toluic Acid.—Since *p*-sulphamido-*o*-toluic acid does not lose any of its nitrogen when boiled with either magnesium hydroxide or caustic soda while amidines lose one atom of nitrogen as ammonia when boiled with magnesium hydroxide and another atom when boiled with caustic soda, it was thought that by boiling successively with these two reagents the product obtained by heating the acid at various temperatures and different lengths of time some indication might be obtained as to the extent of any reaction which might have taken place similar to that observed in the case of *m*- and *p*-sulphamido-benzoic and *p*-sulphamido-*m*-toluic acids, and that in this way the most favorable conditions for heating the acid in larger quantities might be determined.

I. 0.4850 gram heated in a sealed tube two hours at 220°

¹ Die Imido-aether, p. 5.

gave with $\text{Mg}(\text{OH})_2$ 48.59 per cent. nitrogen; with NaOH 42.96 per cent. nitrogen.

II. 0.4484 gram heated in a sealed tube four hours at 220° gave with $\text{Mg}(\text{OH})_2$ 47.71 per cent. nitrogen; with NaOH 40.44 per cent. nitrogen.

III. 0.4999 gram heated in a sealed tube six hours at 240° gave with $\text{Mg}(\text{OH})_2$ 56.80 per cent. nitrogen; with NaOH 23.26 per cent. nitrogen.

From the above tests it appears that two hours' heating at 220° is the most favorable condition for preparing the melt of *p*-sulphamido-*o*-toluic acid.

Preparation of the Melt.—The heating was carried out in a large paraffin bath, the temperature of which could be kept constant to within 2° – 3° for a long time.

Test tubes, each containing ten grams of acid and closed loosely with a cork stopper, were heated for two hours at 220° and then allowed to cool in the air. Unlike the melt from *p*-sulphamido-*m*-toluic acid, that from *p*-sulphamido-*o*-toluic acid showed no signs of deliquescence at all. When cool the tubes were broken and the melt removed. The melt was now a dark, brown, brittle mass, very shiny and resembling sealing wax somewhat. When the tubes were opened there was always a distinct nitrile odor and around the top of each tube was observed a very small amount of a sublimate which had the same melting point as the original acid and, when mixed with the acid, still melted at the same temperature, indicating that the sublimate was unchanged *p*-sulphamido-*o*-toluic acid.

Treatment of the Melt.—The first three melts were worked with the main idea of isolating first any "infusible diamide" which might have been formed. Several portions of the melt were subjected to different methods of treatment, so it might not be out of place to give each method separately.

I. Twenty grams of the melt were ground up in a mortar and extracted with cold water until all the substance had dissolved, giving a reddish brown solution, slightly milky in appearance. Unlike the melts of previous workers, the melt of *p*-sulphamido-*o*-toluic acid was completely soluble in a relatively small quantity of cold water. On standing over-

night, a very small amount of a flocculent substance settled out which was soluble in alkalies and reprecipitated by acids. The amount of the substance was far too small for analysis and I never again obtained any of the substance from the other melts.

The clear filtrate was now evaporated to dryness and extracted with acetone.

a. *Acetone Extract.*—Only a very small portion of the melt was soluble in acetone. On evaporating off the acetone, small, light yellow nodules, having a melting point of 192° – 200° , settled to the bottom. When recrystallized from water, it melted at 165° – 170° . The amount of substance was too small to purify for analysis.

b. *Substance Insoluble in Acetone.*—The greater portion of the melt was insoluble in acetone, so it was crystallized several times from water, when short, prismatic needles were formed, some arranging themselves as rosettes and some as crosses. They melted at 285° – 288° , which is the same as the melting point of acid ammonium p-sulpho-o-toluate (p. 227) and, when mixed with the synthetic acid salt, the melting point was unchanged, proving the identity of the two substances.

II. Thirty grams of the melt was ground up in a mortar with a small amount of cold water, when all the substance went into solution readily. The water solution was extracted three times with ether and on evaporation of the ether extract a few oily drops were obtained which had a distinct nitrile odor and gave off ammonia freely with caustic soda.

The filtrate was evaporated to dryness and extracted with acetone.

a. *Acetone Extract.*—On evaporation of the acetone extract, nothing came down except a black tarry mass from which I was unable to isolate any definite product.

b. *Substance Insoluble in Acetone.*—The part insoluble in acetone was dissolved in water and just enough barium hydroxide added to neutralize the solution, which was then evaporated to dryness and the residue extracted with absolute alcohol to separate the barium salts from other salts.

1. The alcoholic extract, on concentration, gave a white

amorphous powder which gave off ammonia freely with caustic soda. When recrystallized, it came down in prismatic plates and crosses melting at 242° – 248° . It was probably the impure acid ammonium salt.

2. The barium salts, insoluble in alcohol, yielded only a grayish powder which was never obtained pure enough for analysis. In another experiment (see p. 228), half of the solution of the melt in water was neutralized with barium hydroxide and added to the other half of the solution. On concentrating, acid barium *p*-sulpho-*o*-toluate crystallized out.

III. Twenty grams of the melt were next treated according to Nakaseko's¹ plan for the separation of the products of the melt. The melt was ground up in a mortar and extracted three times with ether. The ether extract yielded a few oily drops which had a distinct nitrile odor and gave off ammonia freely with caustic soda. The melt was then extracted four times with acetone, which was considerably colored by the dissolved substance.

a. The acetone extract on concentration yielded only a black tarry mass from which no definite product was isolated.

b. *Portion Insoluble in Acetone.*—The residue, which was about 95 per cent. of the whole melt, was dissolved in 50 cc. of water. The beaker was then set aside in a vacuum desiccator over sulphuric acid and allowed to stand until crystallization began. The substance came down first in the form of an amorphous powder melting at 270° – 274° , evidently impure acid ammonium salt. I tried recrystallization by the above method several times but was never able to get any distinct crystals. I then tried recrystallization from alcohol in a vacuum but was able to get no better results.

Having by the above methods been able to isolate only acid ammonium and barium sulphotoluates, I next treated the melt as follows:

IV. I heated twenty grams of *p*-sulphamido-*o*-toluic acid two hours at 223° . On cooling, the dark brown brittle mass had a distinct nitrile odor. It was dissolved in about 50 cc. of water and digested with charcoal to remove the brown

¹ Diss., Johns Hopkins Univ., 1896. THIS JOURNAL, 47, 429.

color. To the now clear solution of the melt, 0.2 N ammonia was added until it was just neutral. Four hundred cc. of the ammonia was required and as 465 cc. would have been necessary to neutralize the original acid, it is evident that the acidity is practically the same after as before the heating. The neutral solution was concentrated to about one-half its volume and on standing overnight a mass of prismatic crystals came down, so thick that the beaker could be inverted without any of the solution spilling. After four crystallizations, the substance came out in shiny, needlelike, elongated prisms melting at 274° – 276° .5, and when mixed with some of the ammonium 1-carbamido-2-methylbenzene-4-sulphonate described above (p. 232), the melting point was unchanged, this fact, of itself, pointing to the identity of the two compounds.

Analysis of the crystals melting at 274° – 276° .5:

0.2686 gram boiled with $\text{Mg}(\text{OH})_2$ gave ammonia equal to 11.5 cc. 0.1 N acid; and with NaOH gave ammonia equal to 11.5 cc. 0.1 N acid.

		Calculated for $\text{CH}_3\text{C}_6\text{H}_3(\text{CONH}_2)\text{SO}_3\text{ONH}_4$	Found
With $\text{Mg}(\text{OH})_2$	N	6.035	5.99
With NaOH	N	6.035	6.16
Total N		12.07	12.15

So, without a doubt, the substance in the melt that gave this ammonium salt was 1-carbamido-2-methylbenzene-4-sulphonic acid.

After filtering off the prismatic crystals described above, the mother liquor was further concentrated and the whole mass solidified without crystallizing at all. Part of it was dissolved in acetone and a substance melting at 210° – 220° , evidently the diammonium salt of *p*-sulpho-*o*-toluic acid, separated but could not be obtained in pure form. I then dissolved it in 95 per cent. alcohol and let it stand, when transparent needles or elongated prisms grouped in the form of rosettes and melting at 284° – 286° came out. Analysis of this fraction gave 8.18 per cent. nitrogen, which is between the calculated values for the acid, 6.01 per cent., and diammonium, 11.2 per cent., salts, showing very plainly that I had here a mixture of the two salts.

On standing for a day or more, the final mother liquor deposited colorless stout prisms and cubes which melted at 284° – $284^{\circ}.5$.

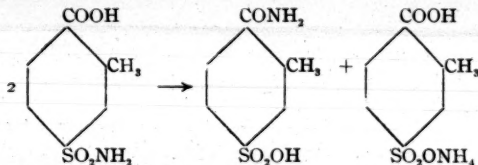
Analysis:

0.3018 gram gave with $\text{Mg}(\text{OH})_2$ ammonia equivalent to 13.00 cc. 0.1 N acid; and with NaOH only a trace.

	Calculated for $\text{CH}_3\text{C}_6\text{H}_4(\text{COOH})\text{SO}_2\text{ONH}_2$	Found
N	6.01	6.03

The final mother liquor was distinctly acid to litmus, showing that the diammonium salt is quickly hydrolyzed to the acid ammonium salt.

Having isolated only acid ammonium sulphotoluate and ammonium 1-carbamido-2-methyl-4-sulphotoluate from the melts, the course of the reaction that takes place when *p*-sulphamido-*o*-toluic acid is heated to 220° for two hours may be represented thus:



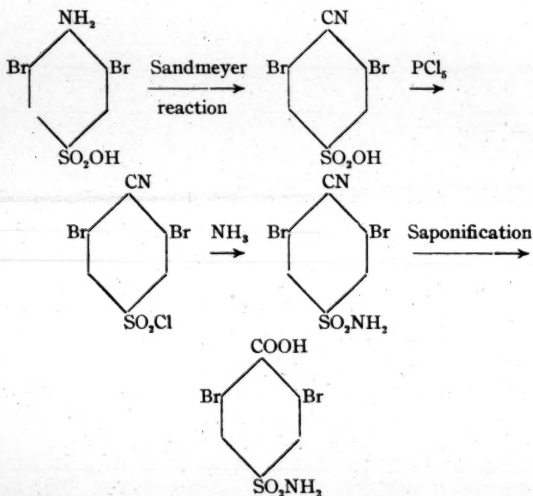
indicating that the methyl group in the ortho position to the carboxyl in *p*-sulphamido-*o*-toluic acid exercises a steric hindrance effect, arresting the reaction at an intermediate stage and preventing entirely the formation of an amidine.

The water necessary for the formation of the acid ammonium sulphotoluate is doubtless furnished by the carbonization of a part of the acid. That the reaction proceeds essentially as represented above is indicated by the fact that the total acidity is practically unchanged and that approximately one-half of the total nitrogen is set free from the reaction product by magnesium hydroxide and the other half by sodium hydroxide (see Experiment I, p. 233).

Having tested out the effect of a methyl group in the ortho

position to the carboxyl, attempts were now made to prepare other compounds with different substituent groups in the ortho position to the carboxyl group in *p*-sulphamidobenzoic acid that the relative steric hindrance effect of different substituent groups might be compared.

Attempt to Prepare 2,6-Dibromo-4-sulphamidobenzoic Acid.—Barium 2,6-dibromosulphanilate was prepared according to the directions given by Heinichen.¹ I hoped now by the following reactions to pass from the 2,6-dibromosulphanilic acid to 2,6-dibromo-4-sulphamidobenzoic acid:



I precipitated the barium from the barium salt with a slight excess of sulphuric acid, filtered off the barium sulphate and subjected the clear solution to the "Sandmeyer Reaction." On concentrating and cooling, a kind of jellylike, greenish mass came down which, when recrystallized from water, deposited a network of long yellow needles. The needles, how-

¹ Ann. Chem. (Liebig), **288**, 269.

ever, were so very soluble in water that I made the barium salt which came out in fine shiny plates forming a fluffy mass. These were purified by recrystallization and dried for analysis, but the ammonia given off by 0.8437 gram of the salt when distilled for three hours with an excess of caustic soda only neutralized 0.6 cc. of 0.1 N acid. From this, it is evident that the salt is either not a nitrile or if it is a nitrile, the two bromine groups in the ortho positions prevent saponification. In view of this fact, further attempts to prepare 2,6-dibromo-4-sulphamidobenzoic acid were abandoned for the time being.

Preparation of o-Nitro-p-sulphamidobenzoic Acid.—An attempt was now made to prepare *o*-nitrosulphanilic acid according to the directions given by Nietzki and Lerch.¹ One part of acetanilide was treated with three parts of fuming sulphuric acid containing 18–20 per cent. of sulphur trioxide. Then two parts of concentrated sulphuric acid were added. The calculated amount of concentrated nitric acid, mixed with an equal volume of sulphuric acid, was dropped in slowly with constant shaking. When cooled, the mixture was poured on ice, when a broth of yellow needles should separate, the acetyl group being split off by the water. In no case, however, was I able to get any yellow needles of *o*-nitrosulphanilic acid by this method, so I turned to another method for preparing *o*-nitro-*p*-sulphamidobenzoic acid.

I began with *o*-nitrotoluene as the starting point and followed Hart's² directions for getting calcium *o*-nitrotoluene-*p*-sulphonate. The calcium salt was changed into the potassium salt by treating it with potassium sulphate and filtering off the calcium sulphate formed. On cooling the filtrate, the potassium salt came out in long, prismatic needles, which were dried and treated with phosphorus pentachloride. On heating the mixture on the water bath, a reaction set in and the whole mass melted to a light yellow liquid, which was washed several times with ice water and then treated with concentrated ammonia until all the substance had gone into solution. On evaporating off the excess of ammonia and decolorizing the solution with charcoal, the amide came out in fine, silky

¹ Ber. d. chem. Ges., 21, 3220.

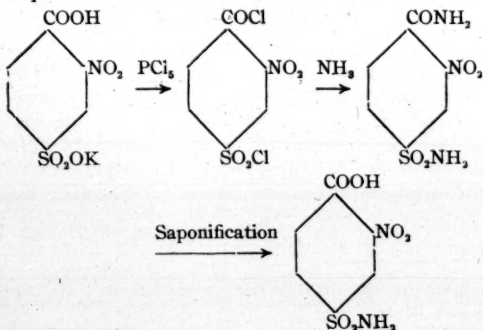
² THIS JOURNAL, 1, 352.

needles melting at 120° – 125° after one crystallization. By repeated crystallization from water, I obtained the amide melting at 142° – 143° , which was comparatively pure.

I thought now that by oxidizing the methyl group to carboxyl I might obtain *o*-nitro-*p*-sulphamidobenzoic acid. Two and sixteen-hundredths grams of the *p*-sulphamido-*o*-nitrotoluene were treated with 0.8 gram of potassium hydroxide to get the amide into solution, then 3.16 grams of potassium permanganate were added in small portions at a time on the water bath. There was a noticeable evolution of ammonia during the oxidation. The oxides of manganese were filtered off and the clear solution acidified with hydrochloric acid but no precipitate was formed. Barium chloride was now added to the solution and 0.18 gram of barium sulphate was obtained, showing that part of the sulphur of the amide had been oxidized to sulphuric acid. The solution was concentrated to crystallization and 1.2 grams of the original *p*-sulphamido-*o*-nitrotoluene were obtained unchanged.

Having been unable to obtain *p*-sulphamido-*o*-nitrobenzoic acid by this method, I next made *p*-sulpho-*o*-nitrobenzoic acid from calcium *o*-nitrotoluene-*p*-sulphonate, according to Hart's directions.¹

From the acid potassium salt I hoped to obtain *o*-nitro-*p*-sulphamidobenzoic acid as follows:



¹ THIS JOURNAL, 1, 352.

I treated 68 grams of the acid potassium salt with 125 grams of phosphorus pentachloride and heated the mixture on the water bath until the whole mass liquefied. After washing about five times with 150 cc. portions of ice water, I obtained the dichloride as a thick yellow oil. This yellow oil was at first treated with concentrated ammonium hydroxide directly in order to prepare the diamide, but the reaction was so violent that I had to use dilute ammonium hydroxide. After evaporating off the excess of ammonia and heating up with charcoal, the diamide came out in fine, silky needles, which, when recrystallized, melted at 226°.

Analysis:

- 0.404 gram gave 0.3777 gram BaSO₄ (Liebig).
- 0.4422 gram gave 0.4276 gram BaSO₄ (Liebig).
- 0.3936 gram gave with NaOH ammonia equivalent to 7.7 cc. 0.1 N acid.

Calculated for		Found	
$\begin{array}{c} \text{CONH}_2 \\ \\ \text{NO}_2\text{C}_6\text{H}_3 \\ \\ \text{SO}_2\text{NH}_2 \end{array}$		I	II
S	13.00	12.84	13.28
$\frac{1}{2}$ N	5.71	2.78	...

From the above analysis for nitrogen, it seems that the nitro group in the ortho position has prevented the saponification of the carbamido group. Five and seven-tenths grams of the diamide were now boiled with an excess of caustic soda for two days, after which the solution was neutralized with hydrochloric acid and digested with charcoal to take out the red color, which is always formed when the diamide is made alkaline. On concentrating the solution, nothing came down until it had gone nearly to dryness, when sodium chloride crystallized out. Nothing else could be isolated from the solution. From the above experiments it is evident that 1-carbamido-2-nitro-4-sulphamidobenzene cannot be saponified by the usual methods, viz., boiling with alkalis, so the method of Bouveault,¹ as modified by Gattermann,² was tried out as follows:

Twenty grams of the diamide were dissolved in a boiling

¹ Bull. soc. chim., 9, 372.

² Ber. d. chem. Ges., 33, 1118.

solution of 50 per cent. sulphuric acid and cooled to about 60°. Then 20 grams of sodium nitrite in 30 cc. of water were gradually led into the solution of the diamide from the bottom by means of a pipette. The solution turned somewhat milky when nearly all the nitrite had been added, but on boiling it cleared up again with the evolution of a gas.

The solution was now concentrated and extracted three times with ether. On evaporating off the ether, a thick oily liquid was left which could not be made to crystallize. This oily extract was dissolved in water and neutralized with barium hydroxide, when a thick precipitate came down. This precipitate was almost completely soluble in hot water, only a small amount remaining undissolved. The barium salt came down from water as an amorphous powder, which I was unable to get out pure enough for analysis because of lack of time.

It is very probable, though, that both the carbamido and sulphamido groups have been decomposed by the nitrous acid, giving *o*-nitro-*p*-sulphobenzoic acid, and the salt obtained by neutralizing the ether extract with barium hydroxide is nothing more than barium *o*-nitro-*p*-sulphobenzoate. The aqueous solution was concentrated to a very small volume, when sodium sulphate crystallized out.

JOHNS HOPKINS UNIV.

VELOCITY COEFFICIENTS OF THE REACTION BETWEEN ETHYL IODIDE AND SILVER NITRATE IN ETHYL AND METHYL ALCOHOLS AND MIXTURES OF THESE SOLVENTS

BY J. N. PEARCE AND OTIS M. WEIGLE

Burke and Donnan¹ made an extensive study of a number of reactions involving alkyl iodides and silver nitrate in ethyl alcohol. They found the reaction to be "pseudobimolecular" in character, i. e., the velocity coefficients of the simple bimolecular equation vary (increase) considerably with the initial concentration of the reacting substances, although they remain fairly constant during the course of any particular reaction.

¹ J. Chem. Soc., 88, 555 (1904).

They found also that the velocity coefficient, k , increases with increasing initial concentration of silver nitrate when the nitrate and the iodide are present in equivalent proportions. Using the same initial concentrations of silver nitrate and varying the proportions of ethyl iodide, the constants, k , are found to decrease with increasing concentration of ethyl iodide. When the iodide is kept constant, the velocity coefficients increase with increasing initial concentrations of silver nitrate. They were not able to explain the variation in the values of k .

The velocity coefficients in ethyl alcohol, using 0.025 N equivalent solutions of silver nitrate and various alkyl iodides, were found to decrease in the following order: isopropyl, ethyl, *n*-propyl, methyl, *n*-butyl, isoamyl and isobutyl iodide, respectively.

The velocity coefficients of four of the iodides, methyl, ethyl, *n*-propyl and *n*-butyl, were likewise determined in methyl alcohol, using 0.025 N equivalents of iodide and silver nitrate.

In every case the velocity coefficients were greater than in ethyl alcohol, the ratio $k_{\text{MeOH}}/k_{\text{EtOH}}$ being approximately equal to 2.

An addition of water to the extent of ten per cent. produced only a slight increase in the value of k . The addition of benzene (10 per cent.), a nondissociating solvent, gave a slightly lower value for k .

In a second paper, Burke and Donnan¹ give the results of further study of the reaction of ethyl iodide and silver nitrate in ethyl alcohol. Their purpose was to study the effect of the reaction products upon the velocity coefficients, and to determine which is the disturbing factor. Experiments proved that this disturbance is not due to ethyl nitrate, or ether, while nitric acid slightly retards the speed. The velocity coefficients are increased by the addition of both calcium and ammonium nitrates. A series of experiments on the amount and rate of formation of nitric acid during the reaction in ethyl alcohol showed that the nitric acid formed is always a constant

¹ Z. physik. Chem., 99, 148 (1909).

percentage (about 70 per cent.) of the amount of silver nitrate which has reacted, and the amount formed is independent of the initial concentrations of the reactants. More acid seems to be formed in mixtures of alcohol and water than in either pure solvent. The velocity coefficient curves for ethyl and methyl iodides in the aqueous alcoholic mixtures show a pronounced maximum near the alcohol end of the curve.

They offer as a tentative suggestion for the variation in the velocity coefficients with change in initial concentrations that "it is the undissociated silver nitrate which reacts and that the decrease in the bimolecular velocity coefficients which might be expected therefrom is compensated by the accelerating action of one of the reaction products." They were, however, unable to determine which of the products is the disturbing factor.

Donnan and Potts¹ made an attempt to determine whether the peculiar behavior already noted is due to the presence of the NO_3 group. They substituted silver lactate for silver nitrate in 60 per cent. alcohol-water solutions. Two series, with different equivalent concentrations of the reactants, were studied. The results showed that the disturbing factor in this case is absent. The ratio of the lactic acid formed to that of the silver lactate used up was the same as for nitric acid and silver nitrate, viz., approximately 70 per cent.

Since free acid is one of the main products when solvents containing a hydroxyl group are used, they decided to carry out the experiments with ethyl iodide and silver nitrate in acetonitrile. No acid, other than a slight trace, possibly due to impurities, was found. The experimental results resembled those obtained when alcohol was used as solvent. The simple bimolecular equation holds for all concentrations studied except the 0.1 N, but the velocity coefficients vary with the initial concentrations of the reacting substances. This would show then that the variation is not dependent upon the formation of acid.

Euler² studied the reaction between chloroacetic acid and

¹ J. Chem. Soc., **97**, 1882 (1910).

² Ber. d. chem. Ges., **39**, 2726 (1906).

silver nitrate in water and in 45 per cent. alcohol-water mixtures. The reaction speed in 0.25 N equivalent solutions was decreased 100 per cent. in the presence of 0.5 N nitric acid.

Senter¹ investigated the reactions between silver nitrate and bromoacetic, α -bromopropionic, α -bromobutyric acids and their sodium salts. Traces of silver bromide added to the reacting mixtures were found to increase the initial velocity coefficients three to six times. The same was found to be true when traces of silver iodide were added to reaction mixtures of methyl iodide and silver nitrate in aqueous solutions. In these experiments the addition of nitric acid shows considerable retarding effect. Benzenesulphonic acid was found to have a still greater retarding effect than nitric acid.

Senter suggests the catalytic action of the silver halides as being the possible cause of the kinetic disturbances observed in reactions in alcoholic solvents.

No measurements of the velocity coefficients of the reactions in the mixed alcohols have been made and very little done with silver nitrate and ethyl iodide in methyl alcohol as solvent. It was thought some interesting facts might be brought to light through a systematic study of the reactions of silver nitrate and ethyl iodide in methyl alcohol, ethyl alcohol, and their binary mixtures.

With this idea in view, these reactions were carried out in pure ethyl alcohol, 75, 50 and 25 per cent. mixtures with methyl alcohol, and pure methyl alcohol.

Materials and Solutions

Ethyl Alcohol.—Ethyl alcohol, after standing for several months over two changes of fresh quicklime, was fractionated and kept over anhydrous copper sulphate until ready for use. It was then fractionated, refluxed with about 30 grams metallic calcium per liter for several hours, fractionated, and immediately refluxed with fused silver nitrate for two hours, and fractionated into dry glass-stoppered bottles. A Glinsky distilling tube and soda-lime or calcium chloride guard tubes were used. Alcohol thus prepared gave a conductivity of 2.4×10^{-7} at

¹ J. Chem. Soc., 97, 346 (1910).

25° C., measured by the Kohlrausch method, with bridge, induction coil and telephone receiver. The Wheatstone bridge wire was calibrated by the method of Strouhal and Barus. The Arrhenius cell, as improved by Jones and Biagham, was used.

Methyl Alcohol.—Kahlbaum's best grade of methyl alcohol was further purified in the same manner as the ethyl alcohol except that the copper sulphate treatment was omitted. The conductivity at 25° C. was found to be 0.8×10^{-6} .

The mixtures of the alcohols were made up by weight, accurate to one-tenth gram per liter.

Silver Nitrate.—Merck's chemically pure silver nitrate was twice recrystallized from a saturated solution in conductivity water by quickly cooling from 60° to 20°. The product was washed with conductivity water, filtered as dry as possible on a Büchner funnel, dried in a toluene bath at 109° for several hours, and cooled in a desiccator, the work being done either at night or in the dark. Several unsatisfactory methods were previously tried, but this gave a product in small dry crystals, showing no sign of coloring.

Ethyl Iodide.—Kahlbaum's best grade of ethyl iodide was washed with dilute sodium hydroxide and water, dried over calcium chloride for two weeks, decanted, and fractionated. This, after nearly eleven months, has shown no tint of color.

Sodium Chloride.—This salt was precipitated by passing pure hydrogen chloride gas into a saturated solution of Merck's guaranteed chemically pure sodium chloride in conductivity water. The fine precipitate was filtered and washed on a Büchner funnel and dried in an electric oven at 110°. The portion used was heated, short of fusion, in a platinum crucible.

Ammonium Sulphocyanate.—Kahlbaum's best grade of good clear crystals was used.

Nitric Acid.—The best obtainable nitric acid, specific gravity 1.42, and free from chlorides, iodides and lower oxides of nitrogen, was kept in the dark in small bottles filled to the neck. Five cc. were used in each titration.

Iron Alum.—Five cc. of a saturated solution, made from good clear crystals, were used in each titration.

Water.—The water was purified by the method of Jones and Mackay:¹ ordinary distilled water was distilled from a large Jena flask containing a small amount of potassium bichromate and sulphuric acid. This was then doubly distilled from a similar flask and solution through a retort containing barium hydroxide and condensed through a block-tin tubing. This water was used in making up all aqueous solutions.

Solutions.—All solutions were made up to volume at 25°. Alcoholic solutions of silver nitrate and ethyl iodide were prepared seven to twenty hours before using, and of such a strength that when equal volumes of the two were mixed the normality desired was obtained. In all titrations 0.025 N silver nitrate and ammonium sulphocyanate solutions were used. The silver nitrate solution was made up by weight and checked against a standard sodium chloride solution by the Volhard method. The precipitate of silver chloride was filtered off before titrating with ammonium sulphocyanate. Since the results agreed very satisfactorily, the other solutions of silver nitrate were made up by weight.

Apparatus and Method

In general, the method used is similar to that followed by all experimenters in the measurement of velocity coefficients of chemical reactions.

All experiments were performed and solutions made up to volume in a constant temperature bath at $25^{\circ} \pm 0^{\circ}.01$. The motor-driven stirrer kept the water in the large granite tank in constant motion. The heat was supplied by means of a sixteen-candle power electric light bulb immersed in the bath and electrically controlled. The thermometer used was certified and graduated in tenths, such that it could easily be estimated to hundredths.

The bottles were suspended in the bath by means of a copper strip framework of clamps constructed for this purpose and which would accommodate twenty bottles at one time.

Every precaution was taken to keep the nitric acid, silver nitrate, ethyl iodide and solutions from the light. The reac-

¹ THIS JOURNAL, 19, 83 (1897).

tion bottles and all solution bottles were thoroughly "seasoned," glass-stoppered, and well protected by sacks of heavy black cloth or paper.

Equal volumes of each solution were quickly poured together, stoppered and shaken thoroughly. Then ten cc. of the mixture, removed by a certified pipette previously warmed in the bath, were introduced into each of several small dry bottles which had been brought to temperature by suspension in the bath. The approximate instant of mixing was taken as the initial time. At previously decided instants, a known amount—always an excess—of 0.025 N ammonium sulphocyanate was quickly poured from an Erlenmeyer flask into the reacting solution to stop the reaction. This mixture was then poured back into the flask, the bottle rinsed three times with chlorine-free distilled water, the solution being diluted to over 100 cc. Five cc. each of a saturated solution of iron alum and of nitric acid were then added and the excess of ammonium sulphocyanate determined by titrating with 0.025 N silver nitrate. From this the amount of silver nitrate remaining in the solution at the instant of stopping the reaction was easily obtained.

One minute is taken as the unit of time. The unit of volume is one cc. The unit of concentration for silver nitrate is the amount of silver nitrate in one cc. of 0.025 N solution; e. g., the concentration of ten cc. of 0.05 N silver nitrate solution is twenty. The concentration of ethyl iodide is expressed in equivalent terms. Unless otherwise stated, all data are the average of duplicate experiments made the same day.

EXPERIMENTAL

Where the reacting substances are present in equivalent amounts, the velocity coefficients, k , are calculated according to the usual bimolecular reaction formula:

$$k = \frac{1}{t} \cdot \frac{x}{A(A - x)}$$

where x is the portion of the silver nitrate transformed in the time t and A is taken as its initial concentration.

In the case of all nonequivalent solutions the following form of the bimolecular equation was used:

$$k = \frac{1}{(A - B)t} \ln \frac{(A - x)B}{(B - x)A}$$

where the characters have the usual meaning.

Table I gives the results of duplicate experiments carried out in each of the five solvents, with equivalent solutions. For any particular reaction, the velocity coefficients show a fairly constant value. However, there is an unmistakable tendency to decrease, especially noticeable as the proportion of methyl alcohol increases, and this decrease is very much greater during the first part of the reaction. On the other hand, the velocity coefficients become larger as the proportion of methyl alcohol increases.

This is strikingly different from results obtained by Burke and Donnan¹ with mixtures of ethyl alcohol and water in which they found a maximum near the alcohol end of the velocity coefficient—solvent curve. It is doubtful if one is justified in considering the mean values of these velocity coefficients, but they will be used to bring out more clearly some general relations.

A variation from the law of averages is shown by a slight sagging of the curve when the mean constants for any one series are plotted against solvents.

By plotting the coefficients for each solvent in a series against time as abscissas, it will be seen that curves for the mixed solvents are drawn towards that in pure ethyl alcohol, thus showing the dominating influence of the latter solvent.

Table II shows the results of a series of experiments similar to those of Table I except that nonequivalent solutions were used, and the same general relations apply here. A comparison of these tables shows that with the same initial concentration of silver nitrate, the velocity coefficients increase as the initial concentration of the ethyl iodide decreases.

A much greater difference may be observed in the values of

¹ *Loc. cit.*

Table I.—Velocity Coefficients. 0.025 N AgNO_3 and $0.025\text{ N C}_2\text{H}_5\text{I}$ in Alcohols as Solvents

100 per cent. ethyl alcohol	75 per cent. ethyl alcohol	50 per cent. ethyl alcohol	25 per cent. ethyl alcohol	100 per cent. methyl alcohol
f	f	f	f	f
0 10.0	0 10.0	0 10.0	0 10.0	0 10.0
9 7.495 0.00371	5 8.12 0.00463	5 7.77 0.00574	5 7.49 0.00670	5 6.96 0.00856
18 6.055 0.00367	10 6.995 0.00430	10 6.67 0.00499	10 6.15 0.00626	10 5.535 0.00807
30 4.97 0.00337	15 6.185 0.00411	15 5.73 0.00497	15 5.145 0.00629	15 4.615 0.00778
50 3.765 0.00328	25 4.96 0.00406	25 4.63 0.00468	25 4.155 0.00563	28 3.385 0.00698
75 2.85 0.00334	40 3.96 0.00381	40 3.64 0.00437	40 3.205 0.00530	51 2.23 0.00683
100 2.12 0.00338	55 3.26 0.00376	55 2.965 0.00431	55 2.56 0.00528	70 1.775 0.00662
	75 2.69 0.00362	75 2.33 0.00438	75 2.08 0.00508	
	100 2.305 0.00334	100 1.895 0.00427	100 1.62 0.00517	

Table II.—Velocity Coefficients. 0.025 N AgNO_3 and $0.025\text{ N C}_2\text{H}_5\text{I}$ in Alcohols as Solvents

100 per cent. ethyl alcohol	75 per cent. ethyl alcohol	50 per cent. ethyl alcohol	25 per cent. ethyl alcohol	100 per cent. methyl alcohol
f	f	f	f	f
0 10.0	0 10.0	0 10.00	0 10.0	0 10.0
10 8.445 0.00407	5 8.90 0.00528	5 8.78 0.00598	5 8.46 0.00804	5 8.345 0.00884
21 7.29 0.00443	10.5 8.145 0.00492	10.5 8.07 0.00521	10.5 7.59 0.00728	10 7.355 0.00891
36 6.875 0.00337	15 7.70 0.00473	15 7.43 0.00566	15 7.03 0.00732	18 6.51 0.00853
55 6.045 0.00386	20 7.32 0.00456	20 7.05 0.00540	20 6.63 0.00710	25 6.073 0.00831
75 5.71 0.00371	26 6.94 0.00447	26 6.645 0.00541	26 6.30 0.00681	32 5.82 0.00792
130 5.285 0.00343	33 6.65 0.00425	33 6.285 0.00542	33 6.005 0.00666	35 5.70 0.00802
200 5.06 0.00374	40 6.295 0.00444	40 6.10 0.00510	40 5.83 0.00628	43 5.495 0.00797
	50 6.05 0.00423	50 5.84 0.00498	50 5.615 0.00607	

NOTE.—c = concentration of silver nitrate.

the velocity coefficients in Tables II and III than was just seen in a comparison of Tables I and II.

It will be noted that, other conditions being the same, a change in the initial concentration of the silver nitrate (Tables IV, VII, and VIII) produces a much greater change in the velocity coefficients than does a similar change in the initial concentration of the ethyl iodide (Tables IV, V, VI).

A comparison of Tables VI and VIII, using the most concentrated solution of the silver nitrate with the weakest concentration of the ethyl iodide, and vice versa, shows that the reaction in the former proceeds much more rapidly than that in the latter, the same amount of silver nitrate being used up in one-third to one-fourth the time required by the corresponding reactions in Table VIII.

According to the law of mass action, the velocity of a bimolecular reaction should be directly proportional to the product of the reacting masses. That other influences than those due to concentration of the reacting substances are at work may be seen by a comparison of Tables VI and VIII. The values of k representing the proportionality between velocities and the products of the active masses vary widely for each solvent.

In order to make certain that no changes were taking place in the apparatus, solutions, or methods during the investigation, a check experiment was carried out with the results as shown in Table X. It is clearly seen that after nearly three months these data could be reproduced quite accurately.

A tabulation of the mean velocity coefficients, Table XI, gives a general survey of the work covered, and may serve to bring out more clearly some of the points already noted. A natural order of tabulation readily shows the increase of the velocity coefficients with increasing initial concentration of silver nitrate. Taking any given concentration of ethyl iodide, e. g., 0.0125 N, the change in the velocity coefficients is considerable. This change is greater as the methyl alcohol increases. Again, consider a series in which the concentration of silver nitrate is the same, e. g., 0.0125 N. The mean constants decrease with increase in the initial concentration

Table III.—Velocity Coefficients. 0.0125 N AgNO_3 and $0.0125\text{ N C}_2\text{H}_5\text{I}$ in Alcohols as Solvents

100 per cent. ethyl alcohol t	75 per cent. ethyl alcohol c	50 per cent. ethyl alcohol i	25 per cent. ethyl alcohol k	100 per cent. methyl alcohol t	75 per cent. methyl alcohol c	50 per cent. methyl alcohol i	25 per cent. methyl alcohol k
0	5.0	0	5.0	0	5.0	0	5.0
11	4.06	10	4.46	0.00242	10	4.205	0.00378
21	3.82	0.00294	23	3.88	0.00251	22	3.675
45	3.25	0.00243	31	3.61	0.00248	31	3.30
70	2.755	0.00237	45	5.26	0.00237	45	2.85
110	2.06	0.00260	65	5.281	0.00258	65	5.239
135	1.695	0.00290	85	2.55	0.00229	85	2.14
170	1.55	0.00262	110	2.20	0.00251	110	1.855
			130	2.00	0.00231	130	1.64
							0.00315
							150
							1.50
							0.00359
							0.00424
							5 4.31
							0.00640
							10 3.90
							0.00564
							25 2.965
							0.00549
							40 2.42
							0.00533
							60 1.945
							0.00524
							90 1.49
							0.00524
							120 1.16
							0.00552

Table IV.—Velocity Coefficients. 0.05 N AgNO_3 and $0.05\text{ N C}_2\text{H}_5\text{I}$

100 per cent. ethyl alcohol t	50 per cent. ethyl alcohol c	25 per cent. ethyl alcohol i	100 per cent. methyl alcohol t	75 per cent. methyl alcohol c	50 per cent. methyl alcohol i	25 per cent. methyl alcohol k
0	20.0	0	20.0	0	20.0	0
9	9.29	4	12.125	0.00812	4	10.36
29	4.72	7	9.41	0.00804	8	7.625
50	3.375	10	8.085	0.00737	12	5.975
70	2.485	15	6.49	0.00694	18	4.56
95	1.995	21	5.285	0.00663	20	4.41
		25	4.86	0.00623	23	4.17
		40	3.63	0.00564	30	3.435
		50	3.075	0.00550	43	2.855
						0.00698
						0.01163
						0.01014
						0.00978
						0.00941
						0.00884
						0.00825
						0.00804
						0.00698

Table V.—Velocity Coefficients. $0.05\text{ }N\text{ AgNO}_3$ and $0.025\text{ }N\text{ C}_2\text{H}_5\text{I}$

t	100 per cent. ethyl alcohol c	k	t	50 per cent. ethyl alcohol c	k	t	100 per cent. methyl alcohol c	k
0	20.0		0	20.0		0	20.00	
10.75	13.13	0.00689	5	14.38	0.00991	7	12.21	0.01452
20	11.585	0.00648	7	13.485	0.00943	10	11.38	0.01417
39	10.51	0.00598	10	12.505	0.00915	13	10.92	0.01370
55	10.17	0.00618	13	11.80	0.00913	16	10.645	0.01319
			18	11.10	0.00899	20	10.525	0.01153
			26	10.555	0.00866			

Table VI.—Velocity Coefficients. $0.05\text{ }N\text{ AgNO}_3$ and $0.0125\text{ }N\text{ C}_2\text{H}_5\text{I}$

t	100 per cent. ethyl alcohol c	k	t	50 per cent. ethyl alcohol c	k	t	100 per cent. methyl alcohol c	k
0	20.0		0	20.0		0	20.0	
5.04	17.695	0.00655	2	18.18	0.01190	2	17.60	0.01754
12	16.335	0.00621	4	17.25	0.01084	4	16.445	0.01743
24	15.555	0.00541	6	16.56	0.01084	6	15.915	0.01633
30	15.31	0.00558	8	16.17	0.01033	8	15.595	0.01567
36	15.175	0.00570	10	15.83	0.01041	10	15.36	0.01578
			14	15.43	0.01045	14	15.17	0.01479

Table VII.—Velocity Coefficients. 0.025 N AgNO_3 and $0.05\text{ N C}_2\text{H}_5\text{I}$

t	100 per cent. ethyl alcohol		50 per cent. ethyl alcohol		100 per cent. methyl alcohol	
	c	k	c	k	c	k
0	10.0		0	10.0	0	10.0
10.07	5.755	0.00312	5	6.50	6.35	4.75
23	3.135	0.00322	9	4.88	9	3.905
34	2.305	0.00289	13	3.92	13.16	2.91
45	1.70	0.00275	18	2.94	19	1.75
60	1.215	0.00255	23	2.51	23.5	1.445
90.04	0.585	0.00245	30	1.905	28	1.17
100	0.56	0.00224	40	1.245	35	0.93
			55	0.765	45.5	0.585
						0.00695
						0.00641
						0.00605
						0.00637
						0.00586
						0.00558
						0.00506
						0.00484

Table VIII.—Velocity Coefficients. 0.0125 N AgNO_3 and $0.05\text{ N C}_2\text{H}_5\text{I}$

t	100 per cent. ethyl alcohol		50 per cent. ethyl alcohol		100 per cent. methyl alcohol	
	c	k	c	k	c	k
0	5.0		0	5.0	0	5.0
4	4.05	0.00270	4	3.92	4	3.57
7	3.64	0.00325	7	3.395	8	2.645
10	3.14	0.00254	10	2.795	13	1.85
17.14	2.34	0.00240	17	1.975	16	1.505
28	1.585	0.00229	23	1.52	20.5	1.20
35.5	1.26	0.00220	30	1.09	24	0.91
63	0.42	0.00235	37	0.835	28	0.78
			45	0.59	32	0.615
						0.00438
						0.00426
						0.00422
						0.00420
						0.00396
						0.00410
						0.00386
						0.00385

Table IX.—Velocity Coefficients, 0.0125 N AgNO_3 and $0.025\text{ N C}_2\text{H}_5\text{I}$

<i>t</i>	100 per cent. ethyl alcohol		50 per cent. ethyl alcohol 50 per cent. methyl alcohol		100 per cent. methyl alcohol	
	<i>c</i>	<i>k</i>	<i>t</i>	<i>c</i>	<i>t</i>	<i>k</i>
0	5.0		0	5.0		
10	3.865	0.00274	5	4.17	0.00380	0.00463
19.08	3.175	0.00265	10.5	3.72	0.00302	0.00466
30	2.63	0.00248	15	3.27	0.00313	0.00472
45	1.88	0.00268	25	2.55	0.00314	0.00453
60	1.56	0.00248	35	2.08	0.00304	0.00465
80	1.05	0.00264	45	1.67	0.00307	0.00432
130	0.425	0.00285	60	1.30	0.00295	0.00437
160	0.225	0.00306	80	0.89	0.00299	0.00440

Table X.—Velocity Coefficients, 0.025 N AgNO_3 and $0.025\text{ N C}_2\text{H}_5\text{I}$

Average of two experiments				A single experiment (check)			
January 13				April 12			
<i>t</i>	<i>c</i>	<i>k</i>		<i>t</i>	<i>c</i>	<i>k</i>	
0	10.0			0	10.0		
9	7.495	0.00371		9	7.48	0.00374	
18	6.055	0.00362		18	6.04	0.00364	
30	4.97	0.00357		30	4.95	0.00340	
50	3.785	0.00328		50	3.80	0.00326	
75	2.85	0.00334		75	2.87	0.00331	
110	2.12	0.00338		110	2.16	0.00330	

Table XI.—Mean Velocity Coefficients of the Reactions between Silver Nitrate and Ethyl Iodide in Alcohols

Silver nitrate	Ethyl iodide	C ₂ H ₅ OH	75 per cent. 25 per cent.	50 per cent. 50 per cent.	25 per cent. 75 per cent.	CH ₃ OH
0.0125 N	0.05 N	0.00239		0.00294		0.00410
0.0125 N	0.025 N	0.00270		0.00314		0.00454
0.0125 N	0.0125 N	0.00286	0.00239	0.00380	0.00380	0.00557
0.025 N	0.05 N	0.00274		0.00417		0.00589
0.025 N	0.025 N	0.00345	0.00396	0.00471	0.00571	0.00747
0.025 N	0.0125 N	0.00380	0.00465	0.00540	0.00695	0.00836
0.05 N	0.05 N	0.00534		0.00681		0.00913
0.05 N	0.025 N	0.00638		0.00921		0.01342
0.05 N	0.0125 N	0.00589		0.01080		0.01625

of ethyl iodide, but the change is much less than in the former case. These facts, already observed by Burke and Donnan¹ in the use of ethyl alcohol as solvent, are now applicable to these reactions carried out in methyl alcohol and in their binary mixtures.

SUMMARY

The velocity coefficients of the reactions of thirty-three of the forty-five possible combinations of concentrations, using 0.05, 0.025, and 0.0125 N solutions of silver nitrate and ethyl iodide in ethyl alcohol, methyl alcohol, and three of their binary mixtures, were obtained.

The velocity coefficients of any particular reaction, calculated by the usual bimolecular equation, show in most cases a fairly constant value. However, they show a decrease as the reaction proceeds and this decrease is more marked in the methyl alcohol and in the mixtures than in the pure ethyl alcohol as solvent.

Time-constant curves for any one concentration in the solvents used show a displacement toward the ethyl alcoholic solvent, thus indicating that this solvent has the greater influence on the reaction.

This is also shown by plotting the mean velocity coefficients against solvents. A slight sagging of the curve shows that the velocity coefficients for the mixtures are a trifle smaller than would be expected from the law of averages.

For the concentrations considered, the coefficients are always greater in methyl alcohol than in ethyl alcohol as solvent.

For any given initial concentration of ethyl iodide in the solvents used, the bimolecular velocity coefficients increase as the initial concentration of the silver nitrate increases. For a given initial concentration of silver nitrate, they decrease as the initial concentration of the ethyl iodide increases, but the change in the coefficients is very much less in the latter case.

The difference in the effects of the two reacting constituents, which is apparently due to the presence of an excess or large

¹ *Loc. cit.*

amount of silver nitrate, increases as the proportion of methyl alcohol in the solvent increases.

PHYSICAL CHEMICAL LABORATORY
STATE UNIVERSITY OF IOWA
May 25, 1912

REVIEWS

A DICTIONARY OF APPLIED CHEMISTRY. By SIR EDWARD THORPE, C.B., LL.D., F.R.S., Professor of General Chemistry and Director of the Chemical Laboratories of the Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. Revised and enlarged edition in five volumes. Vol. II, Chi-Gou. With illustrations. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 786. Price, \$13.50.

The first volume of this new edition has been recently reviewed in these columns, and it is a pleasure to find the second volume appearing so promptly, thus supporting the promise of the early prospectus that the entire work will be complete in two years. As in the first volume, among the names of the contributors are found many who are recognized as world-wide authorities in their respective subjects.

Comparing the alphabetical range of this volume with the same field covered in the old edition, it appears that about sixty-five new articles have been introduced, of which the following are some of the more important: Chromophores and Chromogens; Colloids; Corrosion of Iron and Steel; Cryoscopy; Denaturants; Desiccation and Drying; Diazo Compounds; Diffusion; Egg; Emulsion; Esterification; Fertilizers; Flame; Flash Lights; and Flavanthrene. In these articles, with one or two exceptions, numerous references to the original literature bring the material up to about the end of 1910. The chapter on Colloids is an excellent brief summary of the subject according to the more recent views. Considering the importance of the subject, and the large amount of investigation which has been carried on with reference to the Corrosion of Iron and Steel by Dunstan, Friend, Moody, Cribb, Traube, Whitney, Cushman, Walker, and others, the omission of all references to original papers in this article is to be regretted. Under Esterification, we find a good theoretical consideration of the reaction between an acid and an alcohol. Flame is discussed from the view point of utility, rather than a detailed consideration of the complex chemistry involved in most cases of combustion. Space does not permit of a detailed consideration of each of these new articles, but in each is found a con-

cise and readable treatment of the subject in hand. Besides these new topics introduced, a large amount of new matter has been incorporated in some of the subjects transferred from the old edition; in many cases these have been entirely rewritten, as in the case of Chlorine, Cyanides, Diamond, Disinfectants, Dyeing, Electroplating, Explosives, Fermentation, Formaldehyde, and the excellent discussion of Fuel. Under Chlorine is a very good résumé of the present state of this industry, including the more recent developments in the electrolytic methods, with diagrams of the principal commercial cells. But it is somewhat surprising to read in the opening sentence under Potassium Chlorate, "This salt is always manufactured by the process first indicated by Liebig;" The manufacture by electrolysis is, however, given about half a page at the end of the article, as compared with the nearly three and a half pages devoted to the old lime process. Under hydrochloric acid manufacture no mention is made of the process of Askenazy, or of Masson, by the action of chlorine and steam on sulphuric acid, nor of Roberts' process for direct combination of chlorine and hydrogen, which has been used at Niagara Falls. Since the first edition appeared, the Cyanides have attained great commercial importance, and under this head is found a good digest of the various methods of production. The chapter on Dyeing has been remodeled and the various theories of the process are summed up with the conclusion, "that the attempt to cover all dyeing phenomena by any one simple explanation must fail, and that many factors are concerned, the relative importance of which varies in different cases." For practical purposes the dyestuffs are classified in eight groups: Mordant dyes, acid-mordant dyes, acid dyes, direct dyes, basic dyes, sulphide dyes, vat dyes, and ingrain colors. With each class is given a short outline of the method of dyeing on the different fibers. In the topic "Explosives" is found an extended and up-to-date treatment of the properties, manufacture and testing of these various substances. The section on Fuels includes a discussion of the calorific value and methods for its determination; the composition, properties and mode of occurrence of the various solid, liquid and gaseous fuels; and numerous illustrations of industrial gas producers and methods of purifying and cooling the gas. The general arrangement and make-up of the book is concordant with Vol. I¹ and the same care in editing and publishing is obvious.

F. H. THORP

¹ THIS JOURNAL, 48, 191.

DIE FABRIKATIONEN VON BITTERSALZ UND CHLORMAGNESIUM als Nebenbetriebe der Chlorkalium- und Kaliumsulfat-Fabrikation. Von CHEMIKER DR. PHIL. AUGUST BERGE, früher Betriebsführer der chemischen Fabriken auf "Mecklenburgische Kalisalzwerke Jessenitz." Mit 15 Abbildungen im Text. Monographien über chemisch-technische Fabrikations-Methoden. Band XXVIII. Halle a. S.: Verlag von Wilhelm Knapp. 1912. pp. vi + 61. Price, M. 3.00.

As in the case of each of the previously issued monographs of this series, this booklet is written by an expert, having extensive personal knowledge of his subject. Beginning with a short historical sketch of the development of the Potash Industries at Stassfurt, the author passes to a consideration of the various by-products from potassium chloride manufacture. About one-third of the work is devoted to the details of Epsom salt making from kieserite. Diagrams of the apparatus for dissolving, clarifying, settling, crystallizing and drying the product are included.

The recovery of magnesium chloride, its purification and uses, comprise the remainder of the book. For those having direct interest in these industries the little work contains many valuable hints.

F. H. THORP

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Volume VI. By the Editors and the Following Contributors: W. H. GLOVER, THOMAS A. HENRY, FRANK O. TAYLOR, R. W. TONKIN, FRANCIS H. CARR, SAMUEL S. SADTLER, J. J. FOX, CHARLES E. VANDERKLEED, OLIVER CHICK, EDWARD HORTON, P. J. SAGEMAN, R. WHYMPER. Fourth edition, entirely rewritten. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, B.Sc. Philadelphia: P. Blakiston's Son & Co. 1912. pp. ix + 726. Price, \$5.00.

The present volume of Allen corresponds to Part II of Volume III, published twenty years ago, and comprises about 150 pages of additional matter. The divisions of the book and the authors are: Amines and Ammonium Bases (Davis); Aniline and its Allies (Sadtler); Naphthylamines, Pyridine, Quinoline and Acridine Bases (Glover); Vegetable Alkaloids (Henry); Volatile Vegetable Bases (Taylor); Nicotine and Tobacco (Tonkin); Aconite Alkaloids (Carr); Atropine and its Allies (Carr); Cocaine (Sadtler); Opium Alkaloids (Taylor); Strychnos Alkaloids (Vanderkleed); Cinchona Alkaloids (Chick); Berberine and its Associates (Horton); Caffeine, Tea and Coffee (Fox and Sageman); Cocoa and Chocolate (Whympere).

While the division of the work in this way has the advantage that the subject matter is presented authoritatively from various points of view, it has the disadvantage that it lacks a certain continuity of treatment as compared with the older volume, prepared under the direct supervision of Mr. Allen. This is unfortunate in that the proper correlation of the alka-

loids is lost to a degree, and the general reader could well sacrifice some of the detailed descriptive matter for general methods of separation applicable in practical cases. The book is one for reference on special points rather than a laboratory companion for the busy chemist.

The chapters on the various alkaloids contain a wealth of information, well presented and accompanied by references to the journal literature. The chapter on nicotine and tobacco does not measure up to the standard of some of the others. The last two divisions on the book are treated more from a strictly analytical standpoint, the methods chosen following largely those of the American Official Chemists. Even so, some of the important work which has been done in the country in recent years has been overlooked. In the case of coffee, for instance, analyses of coffee beans made fifty years ago are quoted at length, while the complete analyses made by Lythgoe as associate referee for the A. O. A. C. are not mentioned. In the analyses of cocoa the extensive work done by Winton and his associates at the New Haven Experiment Station is entirely omitted. Dubois' older method for estimating sugars in milk chocolate is given at length, but his later modification, when the unsatisfactory polarization at 86° is obviated, is missing. The discussions and interpretations of analyses, on the other hand, are extremely valuable and make these two of the most helpful chapters in the book. The trained chemist will find in the whole book a great deal of information gathered within easy reach, although a more detailed index would render it more readily accessible.

A. G. WOODMAN

MATERIALS FOR PERMANENT PAINTING. A Manual for Manufacturers, Art Dealers, Artists and Collectors. By MAXIMILIAN TOCH, Municipal Lecturer on Paints, Colors, etc., College of the City of New York, Director of the Chemical Laboratory of Toch Brothers. New York: D. Van Nostrand Co. 1911. pp. 208. Price, \$2.00.

Contents: History of Painting; Pigments Used by the Ancients; Sinopia, the Search for the Master's Secret; Photo-Chemical Deterioration of Oil Paintings; Cause of the Cracking of Paintings and the Remedies; Canvas, Wood and Metal as Foundations; Preparation of Canvas in Commercial Practice; Renovation and Cleaning of Pictures; The School of Impressionism; Volatile Solvents; Picture Varnishes; Driers, Linseed Oil and Other Drying Oils; Classification of the Pigments and Their Description; The Permanent Colors; Pigments Dangerous to Health; Pigments Affected by Coal Smoke, etc.; Water in Tube Colors; Pigments which are Permanent, etc.; Pigments which Dry Slowly; The Failure of Sir J. Reynold's Paintings.

This little volume containing 190 pages, covering the subjects stated in the contents should be of much value to artists and decorators in supplying sound and accurate information pertaining to the art and craft of painting.

Many of the mysteries and some of the fallacies held regarding the work of the early masters are explained by the analyses made by the author of the pigments used in their paintings which have survived the effect of time.

The secret of the permanence of these masterpieces is due to the "survival of the fittest" and shows that permanent colors can be obtained now if the artist is willing to use only these pigments which are known to be lasting.

The chapters on deterioration and cracking of paintings, material and preparation of the foundation furnish a scientific explanation of many failures which can be prevented.

The chapter on "Renovation and Cleaning of Pictures" supplies the theoretical factors to be considered in this important phase of the art but can hardly supplement the knowledge and experience necessary to secure success.

Probably the most valuable information is contained in Chapter XIV, "Classification of the Pigments and Their Description" occupying about one-half of the volume.

In this chapter are listed practically all the artists' colors with a brief description of their origin, characteristics, methods of manufacture. This chapter can be studied to advantage by both the artist and the artisan as it shows a relatively few of the permanent earth pigments can be successfully used to produce practically all the colors required either in the studio or the shop.

It is instructive to note that while 94 pages are needed to list and describe these pigments, two pages only are required to list "The Permanent Colors."

The book is provided with an excellent index and the text and illustrations are such as to form an attractive volume.

S. S. VOORHEES

TESTS OF THE ABSORPTIVE AND PERMEABLE PROPERTIES OF PORTLAND CEMENT MORTARS AND CONCRETES, together with Tests of Damp-Proofing and Water-Proofing Compounds and Materials. By RUDOLPH J. WIG, Associate Engineer-Physicist, and P. H. BATES, Chemist, Bureau of Standards. Technologic Paper No. 3, Bureau of Standards. Washington: Government Printing Office. 1912. pp. 127.

At a time when manufacturers of water-proofing and damp-proofing compounds for use with Portland cement mortars are warning their competitors and prospective customers against the manufacture, purchase or use of similar compounds under penalty of prosecution for infringement, there is pub-

lished by that department of the Government which is devoting its time to the examination and testing of structural materials a bulletin describing a series of tests which seem to indicate that these compounds have very little value for their advertised purpose. Representative samples of all classes of water-proofing and damp-proofing preparations were purchased on the open market and carefully planned and executed tests were made.

The results for absorption and permeability showed that the richness of the mixture and the ratio of coarse to fine material are the chief factors in the permeability which decreases with age and the flow of water, the decrease being less marked in lean specimens. It is concluded that with care in proportioning the aggregate, cements may be water-proofed without the addition of any of these "water-proofing" compounds. Where well graded sand is not obtainable, hydrated lime, clay or a larger proportion of cement may be substituted. The addition of small amounts of hydrated lime or clay does not affect the tensile or compressive strength. See *Chemical Abstracts* for more detailed description of results. More extensive tests are contemplated.

C. N. WILEY

NOTIONS FONDAMENTALES D'ANALYSE QUALITATIVE. Par V. THOMAS, Professeur-adjoint à la Faculté des Sciences de Clermont-Ferrand, et D. GAUTHIER, Chef des Travaux de Chimie à la Faculté des Sciences de Clermont-Ferrand. Paris: Gauthier-Villars. 1912. pp. viii + 326. Price, Fr. 10.

The first two of the three parts into which this work is divided constitute a short treatise on Inorganic Chemistry from the standpoint of Qualitative Analysis. Part I is devoted to a description of the apparatus and operations usually employed in both wet and dry methods. The construction and use of the microscope and spectroscopy are carefully explained.

The second part consists of a fairly comprehensive treatment of the characteristic reactions and salts of the common base- and acid-forming elements. The acids are treated in groups and the means of identification of each pointed out. Oxalic, acetic and tartaric acids are omitted and no mention is made of cyanides or sulphocyanates.

In Part II the separation into groups and subsequent identification of the elements are dealt with. The various methods commonly employed within each group are given and the respective advantages and disadvantages pointed out. Appendix I contains notes on the reagents, Appendix II specific gravity tables, and Appendix III some reactions on the rarer elements.

The book differs materially from those published in this country in recent years in that it contains no analytical tables and no theory. As it is, according to the authors, primarily written for students it seems a questionable procedure to so completely separate theory and practise. Little is said with regard to the delicacy of the various tests given and the quantitative idea is almost entirely lacking.

With good laboratory notes the book should be valuable as an aid in developing independence on the part of the student. As a laboratory manual it is much too indefinite and it is difficult to see how the beginner would approach the subject using this book as a text. *Notions Fondamentales* is an excellent reference book in qualitative analysis and as such should prove a valuable addition to the chemical library.

ELWOOD B. SPEAR

DIE CHEMISCHEN GRUNDLEGEN NACH MENGE, MASS UND ZEIT. VON J. H. VAN'T HOFF. Mit 12 in den Text gedruckten Abbildungen und einem Vorwort von ERNST COHEN. Braunschweig: Druck und Verlag von Friedr. Vieweg und Sohn. 1912. pp. x + 91. Price, M. 4.00.

The examination of this little booklet leaves a feeling of sadness in the hearts of those who are more or less familiar with the contributions to science of this truly great man. This feeling is intensified in those who had the privilege of coming into personal contact with this modest, unselfish and genial nature. This is probably the last work from the pen of him who found chemistry essentially empirical, and who left it well advanced towards becoming a branch of exact science.

The really great and epoch-making developments in chemistry, as in every other branch of science, are due to a few—a very few—master minds. It must be stated that this is one of van't Hoff's lesser contributions to chemical science. As its title implies, it deals with conceptions which are essentially physical, yet physics and chemistry are, after all, only closely allied branches of the one great science of nature. H. C. J.

LABORATORY EXERCISES IN PHYSICAL CHEMISTRY. By J. N. PRING, D.Sc., Lecturer and Demonstrator in Electro-chemistry. Publications of the University of Manchester, Physical Series, No. II. Manchester: The University Press; New York: Longmans, Green & Co. pp. xii + 162. 1911. Price, \$1.25.

The author of this little book states in his preface that it is "designed to meet the requirements of students who wish to follow a laboratory course dealing with some of the applications of physical chemistry." The list of experiments selected by Dr. Pring is quite different from that found in most physico-

chemical laboratory manuals but with the growth of the science of physical chemistry in recent years it is no longer possible to include in a laboratory manual intended for the general student examples of every method used by the physical chemist. The manual is divided into three parts. In the first part seventeen exercises in general physico-chemical measurements, calorimetry and electrochemistry are given, the experiments on the charge and discharge of an accumulator being especially commendable. The second part is devoted to electrolytic preparations of such substances as aniline, azobenzene and potassium chlorate. Pyrometry is the subject treated in the third part of the book, brief but clear descriptions of thermo-electric, radiation and optical pyrometers being given, together with directions for the calibration and use of these instruments.

To include in a physico-chemical laboratory manual exercises on electro-analysis and electro-synthesis seems somewhat inappropriate, but since laboratory manuals are prepared primarily to meet local conditions perhaps it is unfair to criticize the insertion of these topics.

Several errors in the text should be pointed out. On p. 59 we read, "Electrolyse with a P. D. of 2.2 to 2.5 volts and current density 0.5 volts and current density 0.5 to 2 amps. per 100 sq. cms." On p. 67 we find, "Others forms of rotating electrodes. . . ." and again on p. 70, "the following method was worked by Ulsch," and lower down on the same page, "The anode is formed by a thin platinum wire which can be coiled round a glass rod to make rigid." On p. 94 we read, "It is important for this purpose, that the platinum electrodes should be well platinised in order to enable the solution of the gases." On p. 102 we find, "The value was relatively low with all the noble metals and with iron and nickel, but increased with the more electro-positive metals: cadmium, tin, lead, zinc and mercury, amounting in the lead case, to as much as 0.78 volt." On page 117 the following formula is given as that of azobenzene:



In a future edition the author will undoubtedly correct such mistakes as the above which seem to be almost inevitable in the first printing of a book. This manual of Dr. Pring's will be a welcome addition to the list of reference books which have already proven useful in laboratory instruction in physical chemistry.

FREDERICK H. GETMAN